THE ORIENTATION OF CRYSTALLITES IN MOLDED GRAPHITES

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

An extensive investigation of the orientation of crystallites in molded, artificial graphites has been performed. It has been found that the crystallites in molded graphites are usually - but not always - distributed symmetrically about some axis. The symmetry axis has been found to differ frequently from the molding axis, contrary to what has generally been assumed. Furthermore, the direction of the symmetry axis and the degree of orientation have been found to vary somewhat within a given graphite block.

An equation, originally proposed by Pappis, et al., has been found to be suitable for describing the distribution of crystallites about the symmetry axis. The equation involves two unspecified parameters. Specification of the direction of the symmetry axis involves two additional parameters. A technique for evaluating these parameters from experimental data obtained by the Bacon method is presented.

Also presented are recommendations for future research.

THE ORIENTATION OF CRYSTALLITES IN MOLDED GRAPHITES

INTRODUCTION

Virtually all nonpyrolytic artificial graphites are polycrystalline and most have their crystallites preferentially oriented in some fashion. Because many of the properties of graphite crystallites are anisotropic (i.e., directionally dependent), preferential crystallite orientation results in anisotropy of the properties of most bulk graphites. The degree of anisotropy of a graphite determines its suitability for many applications. For example, a spacecraft heat shield, ideally, should have a high termal conductivity parallel to the surface in order to distribute the heat load over its entire area, but a low thermal conductivity perpendicular to the surface to insulate the spacecraft. Thus, a graphite intended for use as a heat shield should be highly anisotropic. On the other hand, such a graphite might be unsuitable as a moderator in a nuclear reactor because of mechanical problems associated with non-uniform expansion due to neutron irradiation. The degree of anisotropy of a given property is related to the degree of crystallite orientation of the graphite (see ref. 2) and, consequently, the degree of orientation is, itself, an important property. Unfortunately, no simple method for describing, completely and unambiguously, the degree of orientation of a graphite is presently available. The purpose of this study was to develop such a method.

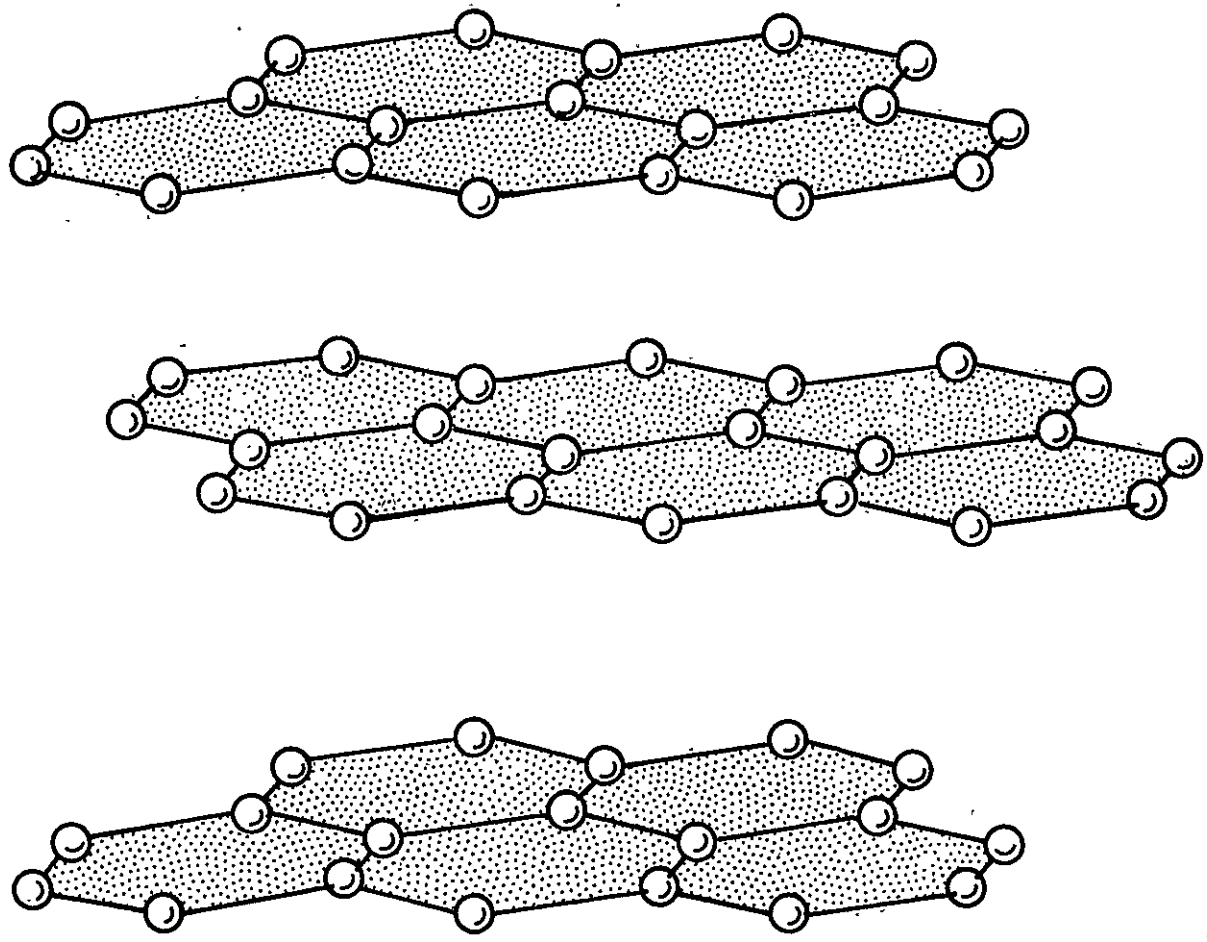
Crystallite orientation in artificial graphites results from an interaction between the structure of the crystallites and the methods

by which graphite bodies are generally manufactured. An extensive treatment of graphite structure and manufacture is given by Nightingale.[11] Harris, Miller, and Craik[9] discuss the effect of these factors on crystallite orientation. A brief discussion of these factors will be given here.

Artificial graphites are generally manufactured from a mixture of a granulated, carbonized filler - such as petroleum coke or lampblack - and a viscous binder with a high carbon-to-hydrogen ratio - such as coal tar pitch. The binder-filler mixture is formed under pressure into billets either by molding into a form or by extrusion through a die. The raw billets are then converted to graphite by heating.

Each grain of filler material contains many regions of partial atomic ordering - incipient crystallites - which, after graphitization, become true crystallites.[9] A graphite crystallite is made up of layers, or "basal planes," each of which constitutes, in essence, a single large aromatic molecule.[19] (See fig. 1.) Bonding within each basal plane is covalent with a bond energy of 150 kcal per mole; bonding between basal planes is due to van der Waals forces and the bond energy is only 1.3 kcal per mole.[11] It is obviously much easier to break bonds between basal planes than within them. Consequently, when filler material is granulated, the grains tend to form in elongated shapes with their major faces parallel to the basal planes of their surface crystallites.[9] In general, the smaller a grain is the more likely it is that most of its crystallites will have similar orientations,

Figure 1.- Crystal structure of graphite.



although the degree to which this is true depends upon the nature and source of the filler material.[9]

When the filler-binder mixture is formed into billets under pressure, the oblong filler grains experience torques which tend to orient them preferentially with respect to the direction of applied force. When the forming process is molding, the most stable orientation of the grains - and, hence, of the basal planes of their constituent crystallites - is perpendicular to the molding direction; in the case of extrusion, the preferred orientation is parallel to the extrusion direction.[11]

The alignment of the crystallites within each grain and of the grains within a graphite body is never perfect, and thus, although one direction is preferred, many crystallites may be found in other directions.[a] Therefore, a complete and unambiguous description of the degree of orientation of a given graphite must include the specification of the relative number[b] of crystallites in every direction.

Crystallite orientation is generally determined experimentally by means of X-ray diffraction. The principle underlying all X-ray studies

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[a]The orientation of a crystallite is usually expressed in terms of an imaginary ray normal to the basal planes of the crystallite rather than in terms of the basal planes themselves, as was done above. This convention will be used henceforth throughout this thesis.

[b]The relative number of crystallites in any direction is the actual number in that direction divided by the number in some reference direction.

of orientation is that the intensity of diffraction from the basal planes[a] oriented in a given direction is proportional to the number of such planes and, therefore, to the relative number of crystallites in that direction. A number of X-ray techniques have been proposed.[1-4,7,13,14] The principal technique utilized in this study is that of Bacon,[2] but some data were obtained by the method of Ali, Fitzer, and Ragoss.[1]

For convenience, this study was limited to molded graphites, but the method of describing orientation which is developed should be applicable to extruded graphites as well.

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[a]The basal planes of graphite are frequently designated in X-ray diffraction work as (002) planes, the numbers in parentheses being Miller indices. Both designations are used interchangeably in this thesis. The diffraction of X-rays from the basal planes is commonly referred to (002) reflection, although this use of the term "reflection" is not rigorously correct.

SURVEY OF PREVIOUS WORK

The earliest systematic study of the orientation of crystallites in graphite was reported by G. E. Bacon.[2] The experimental arrangement for the method of Bacon is illustrated in figure 2. The incident X-ray beam, x, is horizontal; the X-rays are unfiltered CuK radiation. The graphite specimens are thin flat plates approximately 2 × 1 × 0.1 cm, cut with their 1 cm edges parallel to the molding axis, P. Each specimen is aligned so that its 2 cm edges are horizontal and perpendicular to the incident X-ray beam, and its 1 cm edges are tilted from the vertical, z, by 13°.[a]

The graphite specimens are thin enough to allow transmission of a significant fraction of both the diffracted and undiffracted components of the X-ray beam. The diffracted X-rays form a cone with a half-angle of 26° which is twice the Bragg angle for the (002) reflection using CuK radiation. When the diffracted X-rays strike the photographic film - which is perpendicular to the undiffracted X-ray beam and, thus, to the axis of the cone - they form a circular image of varying density on the film. The density of the image at any angle, ξ, is proportional to the number of crystallites at some related orientation within the specimen. The film density is determined at each angle of interest with a microdensitometer.

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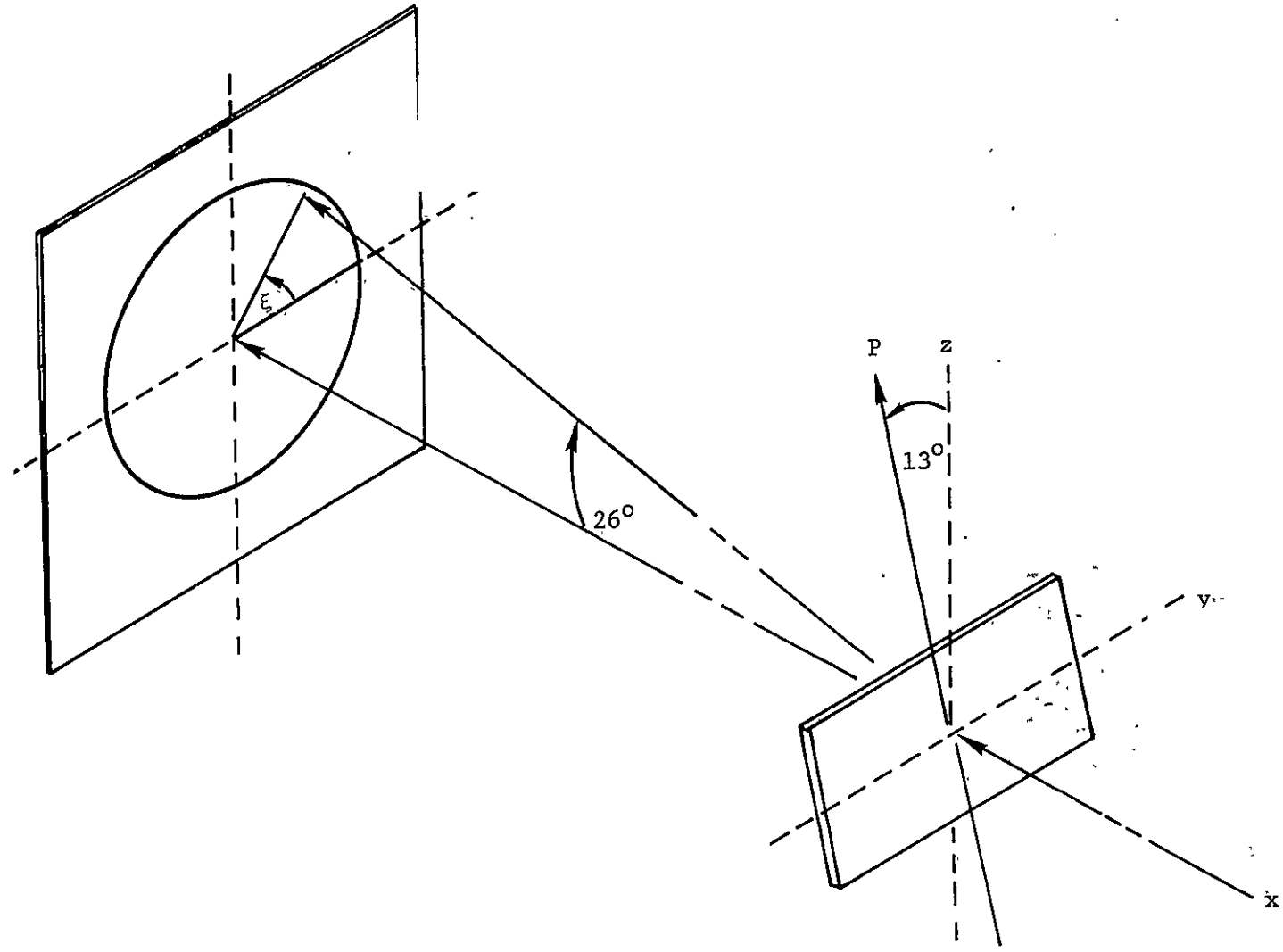
[a]This tilt is necessary so that crystallites with orientations of 0° to 13°, with respect to the forming axis, can be detected. A theoretical discussion of this point is presented in the section, "Theoretical Analysis."

Figure 2.- Experimental arrangement for the method of Bacon.



The main theoretical problem of the Bacon method is the determination of the relationship between angles on the film image and the orientation of crystallites within the graphite specimen. Bacon assumed that the crystallites in artificial graphites are symmetrically distributed about the forming axis. Such a distribution would mean that the only parameter essential to a description of the orientation of the crystallites is the angle, ϕ, which their normals make with the forming axis. Based on this assumption, Bacon derived the following equation relating ϕ and ξ:

$$\cos \phi = \cos^2 77^\circ - \sin^2 77^\circ \sin \xi \qquad (1)$$

For convenience in expressing the angular distribution of crystallites, Bacon defined an orientation function $I(\phi)$ equal to the relative number of crystallites per unit solid angle about the inclination angle ϕ. $I(\phi)$ is usually normalized so that $I(\phi) = 1$ when $\phi = 0$. In practice, $I(\phi)$ is taken as the relative diffraction intensity which, in the case of the Bacon method, is assumed to be equal to $D(\phi)/D(0)$, where $D(\phi)$ and $D(0)$ are the film densities at ϕ and 0°, respectively.

The Bacon method of determining crystallite orientation has the advantage that with one specimen and one exposure it furnishes a continuous, quantitative mapping of $I(\phi)$. The principal disadvantage of the method is that it does not yield diffraction intensities directly and immediately, but requires the intermediate steps of film processing

and microdensitometry. These steps are not only inconvenient, but also constitute possible sources of error.

Ali, Fitzer, and Ragoss[1] contend that a plot of $I(\phi)$ versus ϕ in polar coordinates will always be elliptical within experimental error. Based on this contention, they have proposed that intensity measurements need be made at only two angles, 0° and 90°, since the value of $I(\phi)$ for any intermediate angle can be calculated from the polar equation of an ellipse

$$I(\phi) = \frac{I(0)I(90)}{\left[I(0)^2 \sin^2\phi + I(90)^2 \cos^2\phi\right]^{1/2}} \qquad (2)$$

The experimental procedure proposed by Ali, et al., is as follows: Two flat plates, or discs, are cut so that one is parallel and one is perpendicular to the forming axis of the graphite to be studied. Each specimen is mounted in the flat specimen holder of an X-ray diffractometer and, using a counter-goniometer, the (002) peak of each is determined and recorded on a strip chart recorder. The value of $I(90)$ is taken as the peak height of the specimen whose face is parallel to the forming axis ($\phi = 90^\circ$) divided by the peak height of the perpendicular specimen ($\phi = 0^\circ$). The value of $I(0)$ is taken as one. If intermediate angles are to be investigated, a separate specimen must be cut for each.

The method of Ali, et al., is quite simple if only two specimens need be cut and studied. However, this will be the case only if the distribution of crystallites in the graphite to be studied is, in fact,

both symmetrical and elliptical about the forming axis. Unfortunately, Ali, et al., present only limited experimental substantiation of their assumption and they give no quantitative results.

Harris, Miller, and Craik[9] present polar plots of $I(\phi)$ versus ϕ for four graphites, and in no case is the distribution elliptical. However, all four graphites were extruded rather than molded and three of them were specially prepared in the laboratory rather than commercially manufactured. These results, therefore, do not rule out the possibility that molded commercial graphites possess elliptical distributions. It should be noted that if Ali's assumption of a symmetrical, elliptical distribution is correct, then the normalized value of $I(90)$ constitutes a single parameter which, in conjunction with equation (2), provides a complete specification of the spatial distribution of graphite crystallites.

An alternative one-parameter equation that has been proposed by several investigators is[2,7,8,18a]

$$I(\phi) = \cos^{M}\phi \qquad (3)$$

This equation works fairly well with pyrolytic graphites, but it usually does not work well with molded graphites because they generally have some crystallites with their normals at 90° to the molding axis. Equation (3) assumes that $I(90) = 0$.

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[a]Actually, Bacon proposed the form $I(\phi) = \sin^{M}\phi$ which was intended to be applicable to extruded graphites. The direction of maximum orientation of molded and extruded graphites differs by 90°.

Pappis, et al.,[13] have proposed a variation of equation (3) that overcomes this problem.

$$I(\phi) = A \cos^{M}\phi + B \qquad (4)$$

Unfortunately, these investigators also fail to present any quantitative substantiation of their equation with experimental data. The equation is still of considerable interest, however, and should be compared with the ellipse proposed by Ali, et al., to see if either is clearly superior to the other. Equation (4) can be regarded as a two-parameter equation since, by proper normalization of $I(\phi)$, we may let $A + B = 1$.

Several investigators[1,2,10,12,15] have proposed orientation parameters which attempt to specify the degree of orientation of a graphite with a single number. Such numbers, although useful for some purposes, do not describe the spatial distribution of crystallites. Therefore, they will not be discussed further here.

The assumption of a symmetrical distribution of crystallites about the forming axis has been mentioned repeatedly in this section and in the Introduction, and it is either stated or implied in most papers on graphite orientation.[1,2,9,10,12,13,15,16] Cavin,[10] however, has recently reported experimental results which contradict this assumption. In his investigation, Cavin observed a shift of the symmetry axis from the forming axis by as much as 12°. The experimental technique used by Cavin was a form of a pole[a] figure technique employing a Schultz

[a] A "pole" is an imaginary normal to a crystallographic plane; a (002) pole is thus identical to the basal plane "normal" utilized throughout this thesis.

preferred-orientation apparatus.[17] The basis of this, and all pole figure techniques, is the determination of the diffraction intensity not only as a function of the angle of inclination, ϕ, with regard to some reference axis[a] but also as a function of the aximuthal angle, η, lying in a plane perpendicular to the reference axis.[4] The methods by which pole figures are obtained and interpreted are considerably more complex than the methods proposed by Bacon and Ali, et al. Nevertheless, if the methods of Bacon and Ali are inadequate to determine completely crystallite distributions, the use of a pole figure technique may be necessary. One purpose of this study was to determine whether the Bacon or Ali techniques can be modified so as to detect and account for possible shifts in the symmetry axis and, thus, to yield a complete description of the distribution of crystallites in molded graphites.

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[a] In Cavin's study, the reference axis was the forming axis.

EXPERIMENTAL TECHNIQUES

The methods of Bacon[2] and Ali, Fitzer, and Ragoss[1] were employed exclusively in this study. The vast majority of the data were taken using the Bacon method, but a few checks were made with the Ali method because of its simplicity. Each of these methods is outlined in the previous section. This section will present details of the methods as employed in this study.

The X-ray instrument utilized for both the Bacon and Ali methods was a General Electric Co. XRD-5 with various accessories. The X-rays were nickel-filtered CuKα radiation. The peak tube voltage was 50 kV.

The experimental apparatus used for the Bacon method was a transmission Laue camera with 0.020-inch-diameter pinhole collimator and a 4- by 5-inch film cassette. Ten grades of graphite were investigated by the Bacon method. Three specimens of each grade were studied.[a] The grades studied are listed in table 1 along with certain of their properties.

The specimens, which were 2.5 × 1 × 0.1 cm, were mounted in a specially constructed holder which permitted them to be oscillated horizontally in a plane normal to the incident X-ray beam. The oscillation increased the number of grains irradiated. The period of oscillation was 1 minute and the amplitude was 0.75 inch. The speed

[a]Only two specimens each of grades ATJ and 2D8D were available.

TABLE 1

SOME PROPERTIES OF GRAPHITE GRADES STUDIED

Grade	Filler	Density, gm cm^{-3}	Maximum grain size, mm
ATJ	PC[b]	1.74	0.15
ATJ (G.P.)[a]	PC	1.72	0.15
2BE	PC	1.40	0.15
9RL	PC	1.68	0.08
3499S	PC	1.63	0.08
4007	PC	1.70	0.20
L31	LB[c]	1.66	0.15
2D8D	LB	1.40	0.18
CDG	PC and LB	1.49	0.41
CMB	PC and LB	1.79	0.08

[a]Gas purified.
[b]Petroleum coke.
[c]Lampblack.

of oscillation was kept constant so that all grains irradiated were exposed for the same length of time. The exposure time was 1 hour. Specimens of grade CDG, which is somewhat coarse grained, were exposed in two steps of 1/2 hour each. After the first 1/2 hour, the specimens were raised in the holder so that more grains would be exposed.

The film used was Kodak Type M industrial X-ray film. The films were individually processed with Kodak Liquid X-ray Developer and Replenisher and Kodak Liquid X-ray Fixer and Replenisher. The manufacturer's processing instructions were followed throughout.

The density of the processed film was determined with a Joyce Loebl dual-beam microdensitometer. The films were mounted on a special rotary stage with angular markings to 0.1°. The stage was then rotated to each desired value of ξ and radial scans of the circular diffraction image were made. The result of each such scan was a trace, on ruled paper, of the density versus $\tan 2\theta$.[a] Typical traces are shown in figure 3.

Bacon stated in his paper that the integrated density - the area under the diffraction peaks - is proportional to $I(\phi)$. Ali, et al., and Guentert contend that the peak height and peak area are proportional to each other and to $I(\phi)$ and that the height is preferable to the area since it is easier to measure. Actually, the height and area are not always proportional to each other as is shown in table 2 in which the ratio of the normalized peak heights and peak areas is listed for

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[a] θ is defined as the angle between the incident X-ray beam and the basal planes of the diffracting crystallites. The angle between the diffracted and undiffracted components of the X-rays is 2θ.

Figure 3.- Typical X-ray diffraction peaks.

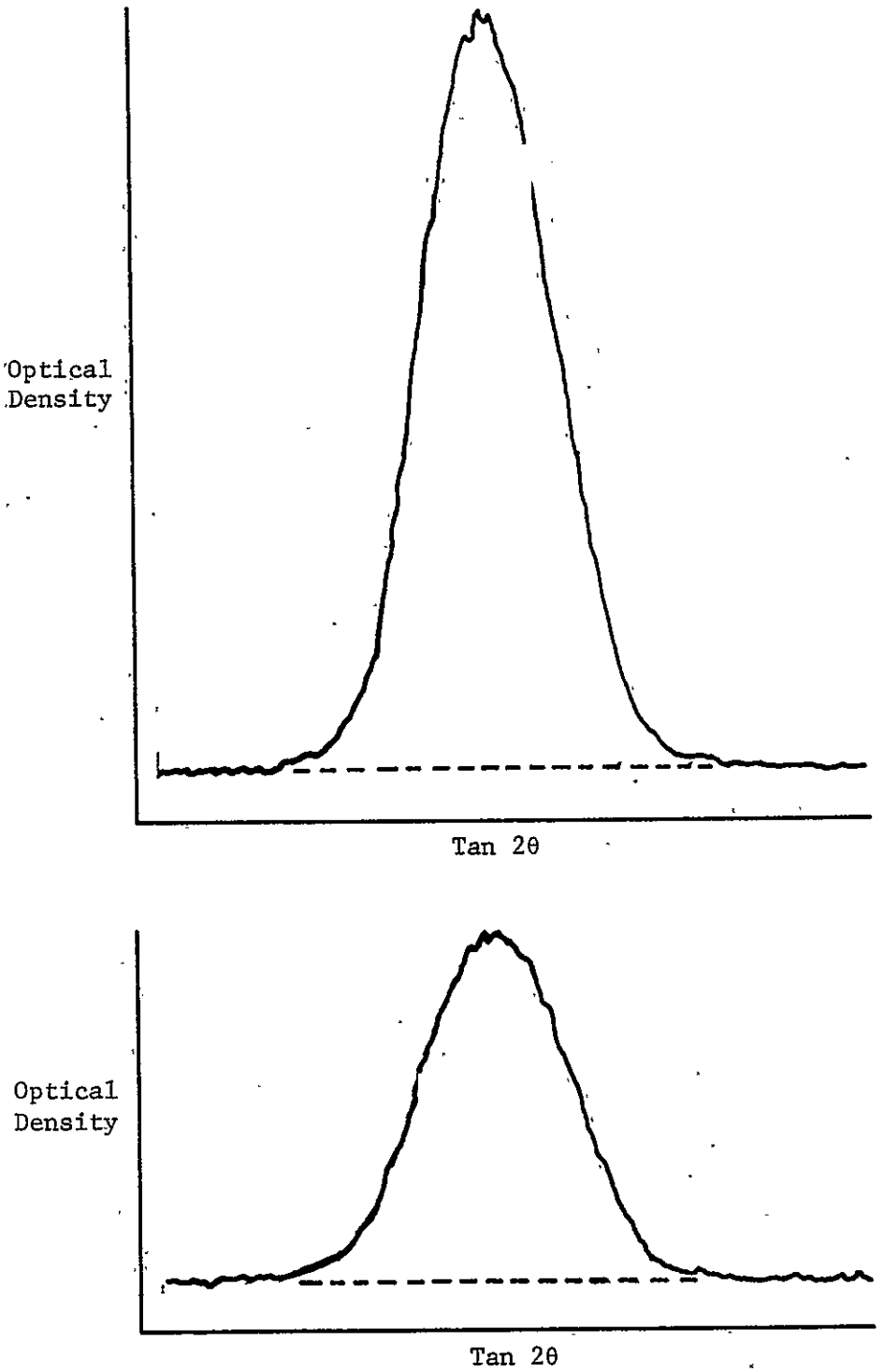

TABLE 2

RATIO OF NORMALIZED PEAK AREAS TO PEAK HEIGHTS

FOR GRADE ATJ

ξ, deg	$I(\phi)_{AREA}/I(\phi)_{HEIGHT}$	
	Spec. No. 1	Spec. No. 2
0	1.06	1.05
10	1.02	1.03
20	1.02	1.02
30	0.99	0.99
40	0.98	0.96
50	0.92	0.92
60	0.93	0.87
70	0.86	0.86
80	0.88	0.88
90	0.88	0.88
100	0.89	0.88
110	0.91	0.87
120	0.92	0.90
130	0.96	0.93
140	0.99	0.94
150	1.02	0.99
160	1.09	1.04
170	1.09	1.01
180	1.11	0.99
190	1.09	1.00
200	1.07	1.04
210	1.01	1.02
220	1.01	0.99
230	1.00	0.96
240	0.96	0.98
250	1.00	0.94
260	0.98	0.95
270	0.96	0.93
280	0.99	0.94
290	0.97	0.96
300	1.00	0.98
310	1.01	0.97
320	1.05	1.04
330	1.05	1.04
340	1.10	1.05
350	1.10	1.06

the two specimens of grade ATJ. It can be seen that the ratio is not unity and, in fact, is not even constant. The variations are too large and systemmatic to be due entirely to experimental error.

The problem of ascertaining the best measure of $I(\phi)$ is complicated by the following facts: (1) The size and shape of a diffraction peak are influenced by other factors in addition to the number of crystallites causing diffraction (see, for example, ref. 5). (2) A molded artificial graphite is not a homogeneous material. It has at least two phases - binder and filler - and more than two phases if two or more fillers are used. The overall diffraction peaks obtained are the sums of the peaks of the individual phases. This problem is treated in some detail by Noda and Inagaki.[12] (3) The abscissa of the diffraction peaks obtained from Bacon films is $\tan 2\theta$ rather than 2θ.

The resolution of this problem was beyond the scope of this study. Furthermore, it was felt that a comparison of the results obtained using peak height and peak area data would be of interest. Therefore, both were measured in this investigation.

The 28 films obtained from the 10 grades of graphite studied were scanned in 10° increments of ξ from 0° through 350°. In addition, one grade - 2BE - was reread every 2.5° of ξ. The heights of the diffraction curves were obtained by subtracting the average background height from the average height of the peak crests, both of which were read directly from the ruled paper.

Three grades of graphite - ATJ, 2D8D, and CMB - were investigated by the Ali technique. The approximate dimensions of the specimens used were 2-3/4 × 1 × 5/16 inch. For each specimen, the value of 2θ was varied continuously over about a 5° range encompassing the Bragg value.[a] The variation was extensive enough to encompass the entire peak as well as some background on either side. The peak area was determined with a planimeter and the height was taken as the peak deflection minus the average of the background deflections.

The peak heights measured in this study have an uncertainty of ±1 to 2 percent[b] except when a dust speck or film blemish caused a spurious deflection at or near the peak crest. In such cases the uncertainty is estimated to be about ±5 percent. The uncertainty in peak areas is considered to be greater than in peak heights because of the increased effect of uncertainties in the baseline. Errors in determining the baseline have a linear effect on the uncertainty of the peak heights but a much greater effect on the uncertainty of the peak areas because of the divergence of the diffraction peak at its base (see fig. 3). Dust specks and film blemishes are also troublesome when areas are being determined. All such spurious deflections were faired

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[a]The goniometer dial of a diffractometer generally reads values of 2θ rather than θ. The Bragg value of 2θ for graphite with CuKα radiation is about 26.5°; the value varies somewhat with crystallite size and degree of graphitization.

[b]The background and peak crests could each be measured to within about half of a line on the ruled paper. Most of the peak heights obtained lie in the range 50 to 100 lines.

through before the areas were determined, but some additional uncertainty was introduced. Overall, the planimeter integrations are estimated to be uncertain to about 2 to 3 percent.

Many factors contribute to the uncertainty in the angular orientation of the specimens, but the major source of uncertainty unquestionably was the cutting process. The Bacon specimens were cut in two steps: First, 1-inch cubes were sawed from the billets as received at this laboratory. The cubes were cut with an angular accuracy of about 2° or better and the pressing direction was clearly marked. The specimens were then cut from the cubes by the Speer Carbon Company under contract to NASA. No estimate of angular uncertainty was furnished by Speer. A value of 2 percent will be assumed since the final cutting of the specimens should not have been any more inaccurate than the sawing of the cubes. All other sources of error contributed less than 1°. Thus, the total angular error in the Bacon specimens should be less than 5°. The Ali specimens were cut in one step at this laboratory; their total angular uncertainty is no more than 2°.

THEORETICAL ANALYSIS

In this section we will consider the implications of assuming that the distribution of crystallites in molded graphites is symmetrical about some axis which is not necessarily coincident with the molding axis. We will then attempt to devise a technique by which (1) the spatial distribution of crystallites in a given graphite can be completely determined from a properly obtained Bacon film image, and (2) the distribution so determined can be expressed, completely and unambiguously, with a minimum number of parameters.

Assume that the graphite specimen shown in figure 2 possesses a symmetry axis having some unspecified direction. Let $\hat{S}$ be a unit vector coincident with the symmetry axis. In the coordinate system shown in figure 2

$$\begin{aligned}\hat{S} &= \cos \alpha_S \hat{i} + \cos \beta_S \hat{j} + \cos \gamma_S \hat{k} \\ &= l_S \hat{i} + m_S \hat{j} + n_S \hat{k}\end{aligned} \tag{5}$$

where α_S, β_S, and γ_S are the angles which the symmetry axis makes with the x, y, and z coordinates axes and l_S, m_S, and n_S are the corresponding direction cosines.

Let $\hat{N}$ be a unit vector normal to the basal planes of some crystallite of interest. In terms of the direction angles α_N, β_N, and γ_N and the direction cosines l_N, m_N, and n_N

$$\hat{N} = \cos \alpha_N \hat{i} + \cos \beta_N \hat{j} + \cos \gamma_N \hat{k}$$
$$= l_N \hat{i} + m_N \hat{j} + n_N \hat{k} \tag{6}$$

The scalar product of the unit vectors $\hat{N}$ and $\hat{S}$ is, by definition, equal to the cosine of the angle between them. But the angle between $\hat{N}$ and $\hat{S}$ is the orientation angle ϕ. Thus,

$$\hat{N} \cdot \hat{S} = l_N l_S + m_N m_S + n_N n_S$$
$$= \cos \phi \tag{7}$$

From the properties of direction cosines, we know that

$$l_N^2 + m_N^2 + n_N^2 = 1 \tag{8}$$

$$l_S^2 + m_S^2 + n_S^2 = 1 \tag{9}$$

If we solve equation (8) for m_N and equation (9) for n_S, we get

$$m_N = \pm \sqrt{1 - l_N^2 - n_N^2} \tag{10}$$

$$n_S = \pm \sqrt{1 - l_S^2 - m_S^2} \tag{11}$$

We may adopt the convention that the vector $\hat{S}$ always has an upward component so that equation (11) becomes positive only.

The condition for (002) diffraction to occur is that the angle between the basal planes and the incident X-ray beam must be the Bragg angle for the radiation used. The Bragg angle for (002) diffraction

using CuKα radiation is 13.25°. If the basal planes make an angle of 13.25° with the incident X-ray beam, their normal must make an angle of either 76.75° or 103.25°, depending on whether the x-component of the normal is positive or negative. If we require that it be positive, then

$$\alpha_N = 76.75^\circ \tag{12}$$

It can be shown from consideration of spherical coordinates that

$$n_N = \sin 76.75^\circ \sin \xi \tag{13}$$

If equations (10) through (13) are combined with equation (7), the following general equation relating ϕ and ξ is obtained:

$$\cos \phi = l_S \cos 76.75^\circ \pm m_S \sin 76.75^\circ \sqrt{1 - \sin^2 \xi}$$

$$+ \sqrt{1 - l_S^2 - m_S^2} \sin 76.75^\circ \sin \xi \tag{14}$$[a]

Note that equation (14) contains two unknown parameters, l_S and m_S, the direction cosines of the symmetry axis with respect to the x- and y-coordinate axes. Bacon, in assuming that the symmetry axis is

[a] The second term on the right-hand side of equation (14) is negative when $90^\circ < \xi < 270^\circ$, otherwise it is positive. This results from the fact that for the diffracted beam to strike the left half of the film, the y-component of the crystallite normal vector must be negative.

coincident with the forming axis, in effect assumed that $\alpha_S = 103.25^\circ$ and $\beta_S = 90^\circ$. This is equivalent to the assumption that $l_S = -\cos 76.75^\circ$ [a] and $m_S = 0$. If these values of l_S and m_S are inserted into equation (13), the result is

$$\cos \phi = -\cos^2 77^\circ + \sin^2 77^\circ \sin \xi \qquad (15)$$

Equation (15) is essentially the equation derived by Bacon; it differs from Bacon's equation only in the sign of the terms on the right. Since we are only concerned with values of ϕ between 0° and 90°, we may require $\cos \phi$ to be positive and rewrite equation (15) as

$$\cos \phi = \left|\cos^2 77^\circ - \sin^2 77^\circ \sin \xi\right| \qquad (16)$$

Equation (16) results in all values of ϕ from 0° to 90° being represented on the film image as is indicated schematically in figure 4(a). Many values of ϕ are represented at several points on the film. Figure 4(b) is a schematic representation of the limiting values of ϕ and ξ if the specimens are aligned vertically rather than tilted by 13°, as specified by Bacon. These values result from applying the condition that $\alpha_S = 90^\circ$, and therefore, $l_S = 0$ to equation (14). It is obvious from figure 4(b) that crystallites with orientation angles between 0° and 13° would not be detected if the specimens were aligned vertically.

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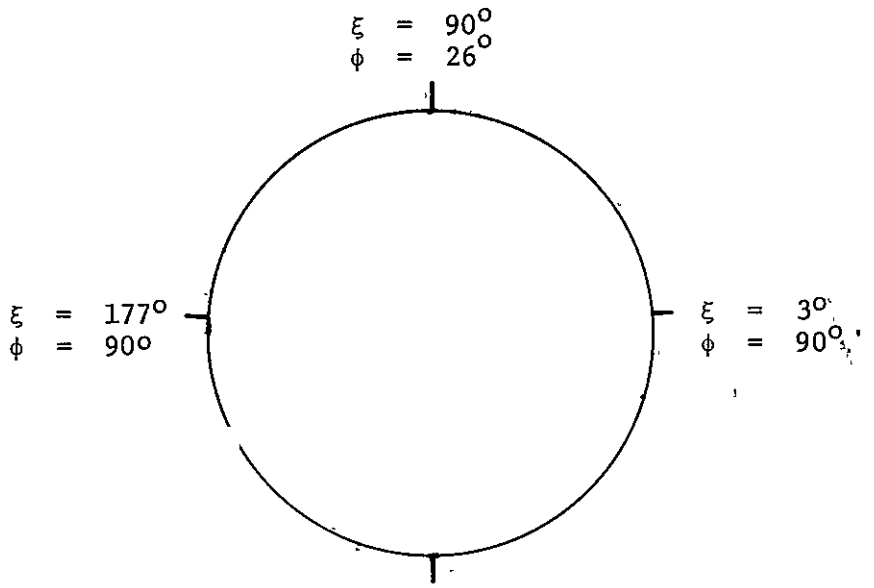
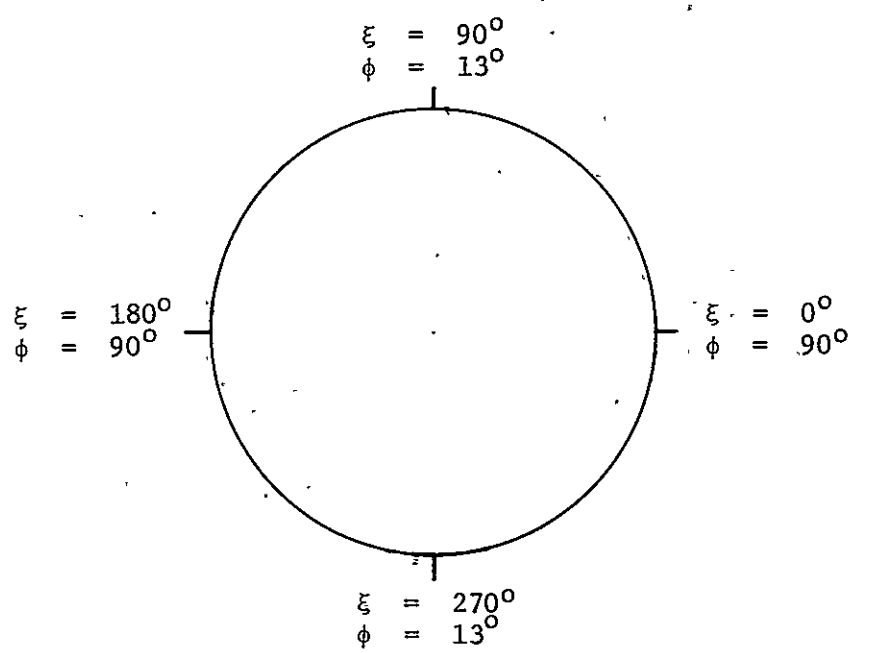
[a] Bacon took the Bragg angle to be 13°, and thus l_S would be $-\cos 77^\circ$.

Figure 4.- Limiting values of ξ and ϕ.



(a) $\cos \phi = \left|\cos^2 77^\circ - \sin^2 \sin \xi\right|$



(b) $\cos \phi \quad \left|\sin 77^\circ \sin \xi\right|$

If Bacon's assumption of the coincidence of the symmetry and forming axes is incorrect, two difficulties arise: (1) the values of l_S and m_S are not known a priori, (2) not all inclinations, ϕ, are necessarily represented on a given film image. These difficulties can be overcome, at least in principle, if a valid closed-form expression relating I and ϕ is known and if sufficient experimental data are available. The procedure involved will be illustrated by considering equation (4), which is $I(\phi) = A \cos^M \phi + B$. Note that ϕ appears only through its cosine. Equation (14) gives $\cos \phi$ as a function of the parameters l_S and m_S and the variable ξ. If equations (4) and (14) are combined, we get

$$I = A\left(l_S \cos 76.75^\circ \pm m_S \sin 76.75^\circ \sqrt{1 - \sin^2 \xi} + \sqrt{1 - l_S^2 - m_S^2} \sin 76.75^\circ \sin \xi\right)^M + B \qquad (17)$$

Equation (17) contains five unknown parameters - A, B, M l_S, and m_S - which can be determined, in principle, if five or more pairs of experimental values of I and ξ are available.[a] Appendix A describes a least squares method for solving nonlinear equations such as equation (17). Appendix B gives a listing of a computer program and related subprograms by means of which the solution can be carried out. This method and program were used in this investigation.

[a]The success of solutions of equation (17) and the subsequently derived equation (19) is dependent on the number and accuracy of the data points available.

Equation (2) can also be combined with equation (14) to yield an equation similar to equation (17). This can be seen more easily by rewriting equation (2) as

$$I = \frac{ab}{\left[a^2 + (b^2 - a^2)\cos^2\phi\right]^{1/2}} \qquad (18)^a$$

This expression may be inserted into equation (14) to yield

$$I = \frac{ab}{\left[a^2 + (b^2 - a^2)(l_S^2 \cos 76.75^\circ \pm m_S \sin 76.75^\circ \sqrt{1 - \sin^2\xi} + \sqrt{1 - l_S^2 - m_S^2} \sin 76.75^\circ \sin \xi\right]^{1/2}} \qquad (19)$$

Equation (19) can be solved by the same least squares method applied to equation (17) to yield the best values of a, b, l_S, and m_S. The requisite computer programs and subprograms are listed in appendix B.

Once the parameters in either equation (17) or equation (19) have been determined, the value of I at any angle ϕ can be calculated (using eq. (14) to relate ϕ and ξ). Thus, it is not necessary that

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[a] The parameters I(0) and I(90) have been replaced by a and b, respectively, for the sake of generality. We have no justification for attaching more weight to experimental values measured at 0° and 90° than to values measured at other angles.

a particular angle be studied experimentally, or even that it be represented on the film image.

The number of parameters actually specified need be only four in the case of equation (17) or three for equation (19), since, by proper normalization, $A + B = 1$ and $a = 1$. The necessary normalization is performed in the programs listed in appendix B. Equations (17) and (19) can be compared by applying each to several sets of experimental data and comparing their variances.

The angle by which the symmetry axis is displaced from the molding axis can be obtained by first representing the molding axis by the unit vector $\hat{P}$ where

$$\begin{aligned} \hat{P} &= \cos 103^\circ \hat{i} + \cos 13^\circ \hat{k} \\ &= -\cos 77^\circ \hat{i} + \cos 13^\circ \hat{k} \end{aligned} \tag{20}$$

and then taking the scalar product of $\hat{S}$ and $\hat{P}$

$$\begin{aligned} \hat{S} \cdot \hat{P} &= -l_S \cos 77^\circ + \sqrt{1 - l_S^2 - m_S^2} \cos 13^\circ \\ &= \cos \delta \end{aligned} \tag{21}$$

The arcosine of $\cos \delta$ is the desired displacement angle, δ.

RESULTS AND DISCUSSION

The data from the 28 Bacon-method diffraction films were reduced using equations (17) and (19). The least-squares values of the various parameters contained in these equations were determined for each set of data using the technique outlined in appendix A and the computer programs and subprograms listed in appendix B. The values of the parameters which were computed are presented in table 3. Also presented in this table are the values of δ, the angle between the symmetry and reference axes,[b] and σ^2, the variance of the data.

Three important observations can readily be made from the results presented in table 4: (1) the values of the parameters obtained using peak heights to represent $I(\phi)$ generally do not agree with the values based on peak areas, even within experimental uncertainty. (2) The values of the parameters computed using equation (17) frequently do not agree with the values obtained using equation (19). (3) The values of δ, in many cases, are too large to be accounted for by experimental error. Each of these points and others related to them will be discussed in this section.

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[a]The values of the parameters a and A are not presented in table I since the data and results were normalized so that $a = 1$ and $A = 1 - B$. Although equations (17) and (19) were solved in terms of the direction cosines l_S and m_S, the direction angles α_S and β_S are easier to visualize; therefore, these angles rather than the direction cosines are presented in table I.

[b]The reference axis was the molding axis within the limits of experimental error.

TABLE 3

LEAST SQUARES VALUES OF ORIENTATION PARAMETERS

(a) Equation (17) - Peak Area Data

Grade	Specimen number	B	M	α_s, deg	β_s, deg	δ, deg	$\sigma^2 \times 10^4$
ATJ	1	0.52	2.8	114	91	11	2.1
ATJ	2	0.52	2.6	122	92	19	1.1
ATJ (G.P.)[a]	1	0.42	3.1	122	89	19	2.2
ATJ (G.P.)	2	0.44	2.9	118	90	15	2.7
ATJ (G.P.)	3	0.42	3.1	114	91	11	3.6
2BE	1	0.35	3.0	111	88	8	19.5
2BE	2	0.31	3.3	103	84	6	1.7
2BE	3	0.33	3.2	101	91	3	8.1
9RL	1	0.52	2.7	106	91	3	2.4
9RL	2	0.50	2.6	120	89	17	2.2
9RL	3	0.52	2.5	122	87	19	2.0
3499S	1	0.59	2.3	117	87	15	2.6
3499S	2	0.52	2.5	108	88	5	2.4
3499S	3	0.52	2.6	111	93	8	2.9
4007	1	0.50	2.9	110	100	12	2.2
4007	2	0.51	2.5	116	78	19	3.0
4007	3	0.43	2.8	112	90	9	2.7
L31	1	N.S.[b]	N.S.	N.S.	N.S.	N.S.	N.S.
L31	2	0.81	2.6	149	95	46	1.9
L31	3	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
2D8D	1	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
2D8D	2	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
CDG	1	0.61	3.0	107	78	13	3.1
CDG	2	0.60	2.5	107	102	12	2.7
CDG	3	0.59	2.6	128	87	25	2.6
CMB	1	0.66	2.2	124	94	22	3.6
CMB	2	0.67	2.1	120	88	17	6.3
CMB	3	0.65	2.3	117	90	14	9.4

[a]Gas purified.
[b]No solution.

TABLE 3.- CONTINUED

(b) Equation (17) - Peak Height Data

Grade	Specimen number	B	M	α_s, deg	β_s, deg	δ, deg	$\sigma^2 \times 10^4$
ATJ	1	0.48	2.6	103	90	1	1.1
ATJ	2	0.51	2.7	109	91	6	0.7
ATJ (G.P.)[a]	1	0.41	3.0	111	89	8	1.8
ATJ (G.P.)	2	0.43	3.0	108	90	5	2.6
ATJ (G.P.)	3	0.38	3.0	107	90	4	1.6
2BE	1	0.34	3.0	104	88	2	21.5
2BE	2	0.29	3.4	98	84	8	2.0
2BE	3	0.31	3.2	95	91	8	7.8
9RL	1	0.48	2.6	97	90	6	1.5
9RL	2	0.49	2.5	109	88	7	1.1
9RL	3	0.51	2.6	108	87	7	1.1
3499S	1	0.56	2.5	101	87	4	2.7
3499S	2	0.50	2.7	97	87	7	1.7
3499S	3	0.48	2.7	101	91	2	0.6
4007	1	0.46	3.0	102	98	8	1.8
4007	2	0.48	2.6	106	79	12	1.3
4007	3	0.41	3.1	101	89	3	1.5
L31	1	0.86	2.2	109	86	8	1.3
L31	2	0.87	1.9	102	91	2	1.1
L31	3	0.86	1.7	115	87	12	1.4
2D8D	1	0.83	1.9	116	88	13	1.8
2D8D	2	0.86	1.7	113	90	10	1.7
CDG	1	0.57	2.5	99	80	11	1.2
CDG	2	0.57	2.9	96	100	12	1.1
CDG	3	0.64	2.3	110	86	9	3.3
CMB	1	0.67	2.4	108	94	7	2.4
CMB	2	0.63	2.4	107	88	4	1.4
CMB	3	0.62	2.7	105	90	2	1.8

[a]Gas purified.
[b]No solution.

TABLE 3.- CONTINUED

(c) Equation (19) - Peak Area Data

Grade	Specimen number	b	α_s, deg	β_s, deg	δ, deg	$\sigma^2 \times 10^4$
ATJ		0.51	109	91	7	4.2
ATJ	2	N.S.[b]	N.S.	N.S.	N.S.	N.S.
ATJ (G.P.)[a]	1	N.S.	N.S.	N.S.	N.S.	N.S.
ATJ (G.P.)	2	N.S.	N.S.	N.S.	N.S.	N.S.
ATJ (G.P.)	3	0.40	108	91	7	17.1
2BE	1	0.37	104	88	2	35.9
2BE	2	0.31	96	84	9	21.6
2BE	3	0.32	95	91	8	25.1
9RL	1	0.51	101	91	2	6.0
9RL	2	N.S.	N.S.	N.S.	N.S.	N.S.
9RL	3	N.S.	N.S.	N.S.	N.S.	N.S.
3499S	1	0.59	112	87	10	5.4
3499S	2	0.52	102	88	2	6.8
3499S	3	0.52	105	93	4	8.3
4007	1	0.50	105	100	11	6.7
4007	2	0.52	111	77	16	7.0
4007	3	0.44	105	90	2	12.1
L31	1	N.S.	N.S.	N.S.	N.S.	N.S.
L31	2	N.S.	N.S.	N.S.	N.S.	N.S.
L31	3	N.S.	N.S.	N.S.	N.S.	N.S.
2D8D	1	N.S.	N.S.	N.S.	N.S.	N.S.
2D8D	2	N.S.	N.S.	N.S.	N.S.	N.S.
CDG	1	0.60	105	77	13	3.7
CDG	2	0.60	103	102	12	4.6
CDG	3	N.S.	N.S.	N.S.	N.S.	N.S.
CMB	1	N.S.	N.S.	N.S.	N.S.	N.S.
CMB	2	0.67	115	87	13	6.7
CMB	3	N.S.	N.S.	N.S.	N.S.	N.S.

[a]Gas purified.
[b]No solution.

TABLE 3.- CONCLUDED

(d) Equation (19) - Peak Height Data

Grade	Specimen number	b	α_s, deg	β_s, deg	δ, deg	$\alpha^2 \times 10^4$
ATJ	1	0.48	98	90	5	8.1
ATJ	2	0.51	104	91	1	5.6
ATJ (G.P.)[a]	1	0.42	105	90	2	11.0
ATJ (G.P.)	2	0.43	103	90	0	10.6
ATJ (G.P.)	3	0.39	100	91	3	15.6
2BE	1	0.35	98	88	6	38.1
2BE	2	0.28	94	83	11	21.6
2BE	3	0.30	92	91	11	25.3
9RL	1	0.47	94	90	9	8.6
9RL	2	0.49	103	88	3	8.5
9RL	3	0.51	103	87	4	6.4
3499S	1	0.55	98	87	6	6.2
3499S	2	0.49	94	87	9	6.2
3499S	3	0.48	97	91	6	7.6
4007	1	0.45	98	98	10	6.8
4007	2	0.49	100	78	12	8.1
4007	3	0.40	96	88	7	11.4
L31	1	0.86	108	86	7	1.3
L31	2	0.87	101	91	2	1.1
L31	3	0.87	111	88	9	1.5
2080	1	0.83	112	88	9	1.9
2080	2	0.87	110	91	7	1.8
CDG	1	0.56	96	79	13	4.5
CDG	2	0.55	94	100	13	2.1
CDG	3	0.64	107	86	6	4.3
CMB	1	0.67	105	94	5	2.8
CMB	2	0.63	103	88	2	3.0
CMB	3	0.61	102	90	1	2.7

[a]Gas purified.
[b]No solution.

The fact that the peak height and peak area data generally do not yield the same values for the various orientation parameters conflicts with the assumption of Ali, et al.[1], and Guentert[7] that they are equivalent measures of $I(\phi)$. Although this investigation did not attempt to resolve the question of which is, theoretically, the better measure of $I(\phi)$, the peak height data have been shown to be more consistent. For example, every one of the 56 cases listed in table 3 which involve peak height data converged to a valid solution, whereas 17 of the 56 cases involving peak area data failed to converge. Also, the average variance of the cases involving peak heights is less than the average for the cases involving areas by a factor of 0.81.[a]

Similar comparisons can be used to show that equation (17) yields more consistent results than does equation (19). All but four cases involving equation (17) converged, but 13 cases involving equation (19) did not converge. The average variance using equation (17) is only 0.31 of the average variance using equation (19). Furthermore, the individual variance for equation (17) is smaller in every case except one, for which it is equal to that obtained with equation (19). These results indicate that the form of equation proposed by Pappis, et al.[13], is better able to describe the spatial distribution of graphite crystallites than is the elliptical form proposed by Ali, et al.[1].

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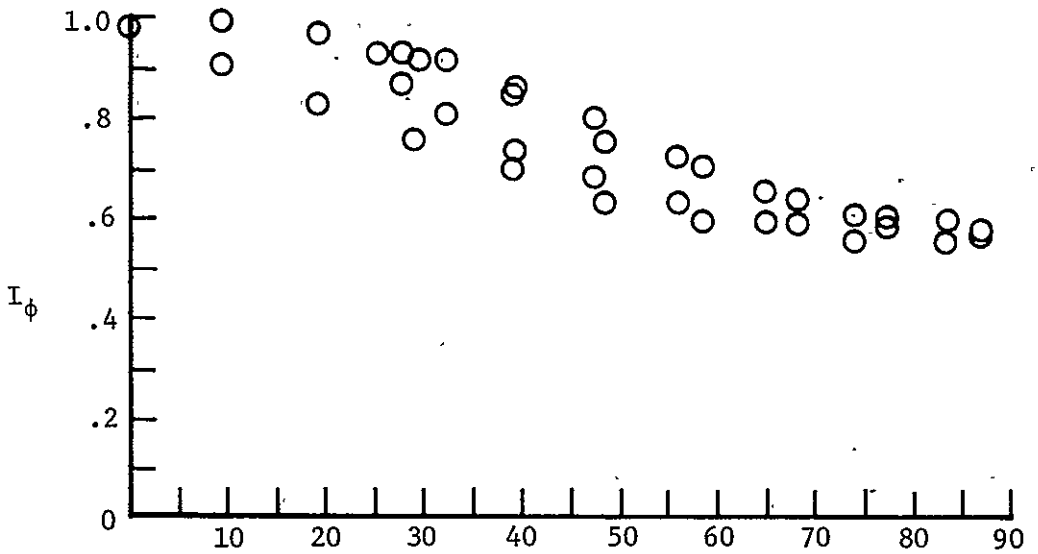
[a]The average variances mentioned here and in the next paragraph do not include the variances of specimens No. 1 and 2 of grade 2BE, which are believed to be atypical. This point will be discussed later in this section.

Perhaps the most significant observation to be made from table 3 is that in well over half of the cases the value of δ is greater than 5°, which is the estimated maximum angular error. In several cases, δ is more than 10°. Thus, significant angular differences between the pressing axis and the experimentally determined symmetry axis exist in many of the specimens investigated. This corroborates the finding of Cavin[3] and contradicts the assumption of Bacon[2] and others.[1,9,10,12,13,15,16]

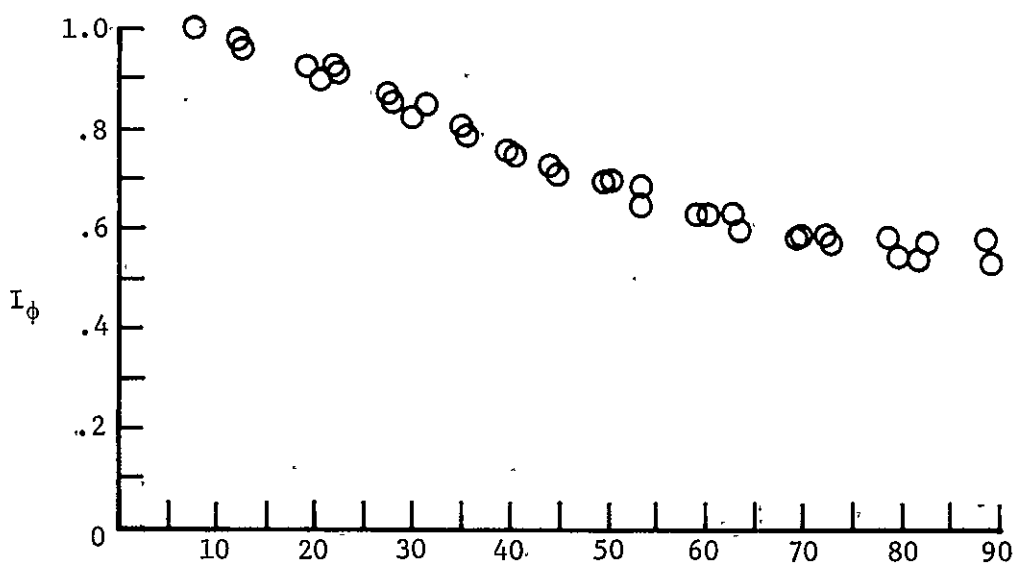
The importance of experimentally determining the symmetry axis and using it, rather than the pressing axis, as the reference axis for specifying the orientation angle, ϕ, is illustrated by figure 5. In this figure the peak height data of film No. 201 are plotted in the following two ways. In part (a), ϕ is referred to the pressing axis; in part (b), ϕ is referred to the computed symmetry axis. It is obvious that the data points are much less scattered when ϕ is referred to the symmetry axis.

It is noteworthy that δ is generally not constant among the three specimens of each grade of graphite. These variations in δ are somewhat confused by the fact that for each specimen as many as four values of δ were obtained which generally differ among themselves. The most consistent values of the various parameters appear to be those obtained from equation (17) using peak heights. If this set of values of δ is considered, angular differences of 5° or more exist among the specimens of 6 of the 10 grades studied. It appears that the symmetry axis of a graphite body does not necessarily have the same direction at all points within the body. Furthermore, the degree of orientation was also

Figure 5.- Iϕ vs. ϕ for graphite grade CDG.



(a) $\cos \phi = \cos^2 77^\circ - \sin^2 77^\circ \sin \xi$



(b) $\cos \phi = \cos 77^\circ \cos \alpha_s \pm \sin 77^\circ \cos \beta_s (1-\sin^2 \xi)^{\frac{1}{2}}$

$+ \sin 77^\circ (1 - \cos^2 \alpha_s - \cos^2 \beta_s)^{\frac{1}{2}} \sin \xi$

found to vary throughout a graphite body since the parameters b, B, and M generally vary somewhat among the specimens within a given grade. It is not known why the direction of the symmetry axis and the degree of orientation vary within a graphite body, but the answer probably involves an uneven distribution of forces within the body during the forming process. Unfortunately, the positions of the specimens within the body were not noted and, thus, no patterns regarding the variations can be ascertained.

Two of the specimens of grade 2BE behaved quite differently from the other specimens tested in that the variances associated with them were abnormally high. Furthermore, the deviations between the experimental and calculated values of $I(\phi)$ (based on the least-squares parameters) were not random. This is shown in table 4. The possibility was considered that perhaps the values of the orientation parameters obtained were not the true least-squares values, but rather were spurious values to which the solutions of equations (17) and (19) had converged. Convergence to unreasonable solutions sometimes occurs with the technique used if the initial values of the parameters chosen are too far removed from the correct values. To check for this, the initial values of the parameters were systematically varied over a wide range, but no solution other than that presented in table 4 was obtained. The three films for this grade were then reread at intervals of 2.5° in ξ to minimize the effects of errors in the individual data points. The data were reduced *in toto* and also using only every fourth data point so that the increment of ξ was 10°. Only equation (17)

TABLE 4

PERCENT DEVIATION OF PEAK HEIGHT DATA FOR

GRADE 2BE

ξ, deg	$100\,\frac{(I(\phi)_{CALC} - I(\phi)_{EXP})^a}{I(\phi)_{EXP}}$		
	Spec. No. 1	Spec. No. 2	Spec. No. 3
0	16.6	5.6	13.2
10	13.0	2.3	10.4
20	10.1	-1.0	5.1
30	9.2	-0.7	5.2
40	12.2	1.5	3.7
50	12.2	4.0	7.1
60	9.9	1.2	5.2
70	8.9	-0.5	5.0
80	5.3	0.2	2.5
90	-0.3	-0.4	-1.0
100	-5.2	1.0	-2.2
110	-7.2	-1.6	-3.6
120	-10.1	-1.1	-4.4
130	-10.8	-3.6	-3.6
140	-11.4	-6.2	-4.4
150	-11.8	-5.3	-9.3
160	-11.7	2.5	-7.0
170	-7.3	6.9	-1.8
180	-5.4	1.9	0.1
190	-9.9	-1.3	-6.2
200	-8.7	-5.0	-10.9
210	-10.3	-2.6	-10.5
220	-6.4	-0.9	-6.1
230	-4.2	0.2	-4.4
240	-3.9	1.8	-1.3
250	-3.7	-1.3	-2.0
260	-2.5	-1.9	-1.4
270	-1.0	-1.5	-0.2
280	2.3	1.0	0.5
290	4.5	3.7	-0.1
300	7.0	4.3	6.5
310	8.8	0.0	7.7
320	8.9	-3.3	5.6
330	8.7	-2.5	1.9
340	8.2	2.9	5.9
350	14.1	3.0	6.8

[a] Values of $I(\phi)_{CALC}$ are based on equation (17).

was used. The results are presented in table 5. It can be seen that no significant improvement in the variance is obtained by considering the additional data points.[a] Apparently, the distribution of crystallites in specimens No. 1 and 2 of grade 2BE is not truly symmetrical about any axis. Specimen No. 2 from the same block of graphite does, however, exhibit a symmetry axis. The cause of this behavior is probably related to the cause of the variation of the direction of the symmetry axis but is not presently known. In any event, it appears that the results for a sample taken at one location in a block of commercial graphite do not, necessarily, apply at other locations withir the block.

It should be clear from the above discussion that the Ali method cannot be expected to give more than a rough approximation of crystallite orientation, since this method involves two fairly large samples which must, necessarily, be cut from different locations, and also since the method depends upon the assumption of an elliptical distribution of crystallites, which has been found not to be correct. A comparison of Ali measurements of $I(90)/I(0)$ on grades ATJ, 2D8D, and CMB with the values of B^b for these grades is given in table 6. As expected, the results do not agree very well.

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[a]Note, also, that the values of the various orientation parameters are not significantly changed by considering the additional data points. Comparison of the values in this table with those in table 2(b) illustrate the reproducibility of the technique used.

[b]The orientation parameters b and B are essentially least-squares estimates of the true value of $I(90)/I(0)$.

TABLE 5

ORIENTATION PARAMETERS FOR GRADE 2BE USING

PEAK HEIGHT DATA AND EQUATION (17)

Specimen number	$\Delta\xi$, deg	B	M	α_s, deg	β_s, deg	δ, deg	$\sigma^2 \times 10^4$
1	2.5	0.34	2.9	105	87	3	18.6
1	10.0	0.34	2.9	105	88	3	20.7
2	2.5	0.29	3.4	97	84	8	2.0
2	10.0	0.30	3.4	97	84	8	2.1
3	2.5	0.31	3.2	95	90	8	6.2
3	10.0	0.31	3.2	95	90	8	7.4

TABLE 6

COMPARISON OF RESULTS OF ALI AND BACON METHODS

(a) Peak Area Data

Grade	I(90)/I(0), Ali	B, Bacon[a]
ATJ	0.56	0.52
2D8D	0.96	N.S.[b]
CMB	0.68	0.66

(b) Peak Height Data

Grade	I(90)/I(0), Ali	B, Bacon[a]
ATJ	0.57	0.50
2D8D	0.99	0.85
CMB	0.52	0.64

[a]Average least squares solution to equation (17) for all specimens of the grade.

[b]No solution.

CONCLUSIONS AND RECOMMENDATIONS

The results of this investigation lead to the following conclusion

1. Most molded, artificial graphites possess an axis about which their crystallites are symmetrically oriented. However, there does not have to be a symmetry axis in all such graphites as indicated in this investigation by grade 2BE.

2. The symmetry axis of a molded graphite does not necessarily correspond to the forming axis and, in fact, frequently does not.

3. The degree of crystallite orientation, the direction of the symmetry axis, and, in fact, whether or not a symmetry axis even exists, can vary from one location to another within a graphite body.

4. The equation $I = A \cos^{M}\phi + B$ is capable of describing the angular distribution of crystallites about the symmetry axis within the limits of experimental error. This equation is more precise than the polar elliptical equation proposed by Ali, Fitzer, and Ragoss.

5. The angle, ξ, on a Bacon diffraction film is related to the orientation angle, ϕ, through the equation

$$\cos\phi = l_S \cos 76.75^\circ \pm m_S \sin 76.75^\circ \sqrt{1 - \sin^2\xi}$$

$$+ \sqrt{1 - l_S^2 - m_S^2} \sin 76.75 \sin\xi$$

where l_S and m_S are the direction cosines of the symmetry axis to which ϕ is referred.

6. The parameters B, M, l_S, and m_S constitute the minimum set of parameters necessary to specify completely the orientation of crystallites in molded, artificial graphites.

7. The height of a diffraction peak is not necessarily proportional to the area under the peak. Consequently, values of the orientation parameters based on peak height data frequently do not agree with the values obtained using peak area data. The precision of peak height data is generally greater than that of peak area data with the techniques employed in this study.

The following recommendations are made for future work:

1. The accuracy with which the direction of the symmetry axis can be determined by the technique proposed in this thesis should be checked. One possible method would involve a specimen holder with two degrees of rotation. First, a specimen would be aligned as specified by Bacon, and the direction of the symmetry axis would be determined as described herein. Then the specimen would be rotated so that the symmetry axis replaced the pressing axis. A second X-ray film would be exposed and δ would be determined. If the theoretical method presented herein is valid, δ should be quite small.

2. A comprehensive study of the factors affecting crystallite orientation should be undertaken with the twin goals of (a) understanding the orientation characteristics of existing graphites and (b) making possible the manufacture of future graphites with a wide range of orientation properties which are consistent throughout the graphite body.

3. A reliable measure of $I(\phi)$ should be determined.

4. The precision of the Bacon method should be increased either by using a very fine grain film, such as Kodak Type R or by using a moving counter, rather than film, as the detector. A counter detector would eliminate the delay and error caused by film processing and microdensitometry. An experimental arrangement involving a counter detector which is adaptable to the Bacon method is described in reference 14.

APPENDIX A

Consider a variable, r, which is an explicit function of some other variable, t, and of u coefficients, c_j

$$r = r(c_1, c_2, \ldots, c_u, t) \tag{A1}$$

If equation (A1) is linear with respect to the coefficients it may be rewritten as

$$r = \sum_{j=1}^{u} c_j \lambda_j(t) \tag{A2}$$

If v pairs of values of r and t are known they may be substituted into equation (A2) to yield the family of equations

$$r_i = \sum_{j=1}^{u} c_j \lambda_j(t_i) \qquad i = 1, 2, \ldots, v \tag{A3}$$

The v equations represented by (A3) may be written as the matrix equation

$$R = \Lambda C \tag{A4}$$

where $R = [r_i]$, $C = [c_j]$, and $\Lambda = [\Lambda_{ij}] = [\lambda_j(t_i)]$

If $v = u$, equations (A3) or equation (A4) can be solved uniquely for the values of c_j by Cramer's Rule[a]. However, if $v > u$ the determination of the coefficients is overspecified, that is, various

[a]Provided that $|\Lambda| \neq 0$ where $|\Lambda|$ is the determinant of the matrix Λ.

combinations of u of the equations (A3) can be solved and each will yield a different set of values for the coefficients. No one set of such solutions is preferable to any other set. However, a statistically preferred set of values can be obtained by applying the method of least-squares[a]. Using this method it can be shown[20] that the best solution for the coefficients, c_j, are the elements of the matrix $\bar{C}$ given by the equation

$$\bar{C} = (A^T A)^{-1} A^T R \tag{A5}$$

The coefficients in equation (A1) can be determined even if the equation is nonlinear by linearizing it as its Taylor series expansion, truncating all terms higher than first order.

$$\Delta r \simeq \sum_{j=1}^{u} \left(\frac{\partial r}{\partial c_j}\right)^0 \Delta c_j \tag{A6}$$

where $\Delta r = r - r^0$ and $\Delta c_j = c_j - c_j^0$. The superscripts on the coefficients refer to approximate values about which the expansion is performed. Superscripts on the dependent variable and its partial derivatives indicate evaluation using the approximate coefficients.

If v pairs of values of r and t are known, equation (A6) generates the family of equations

$$\Delta r_i = \sum_{j=1}^{u} \left(\frac{\partial r}{\partial c_j}\right)_i^0 c_j \qquad i = 1, 2, \ldots, v \tag{A7}$$

---

[a]The method of least-squares yields the "best" statistical solution that can be inferred from a set of data providing the errors in the data are assumed to be normally distributed.

$$\Delta R = \Delta A \, \Delta C \tag{A8}$$

Equation (A8) is equivalent to equation (A4) and, thus, the equivalent least-squares solution is

$$\Delta \bar{C} = (\Delta A^T \, \Delta A)^{-1} \, \Delta A^T \, \Delta R \tag{A9}$$

The values of c_j are obtained from the elements of $\Delta \bar{C}$ by means of the relationship

$$c_j = \Delta \bar{c}_j + c_j^o \tag{A10}$$

Since the higher order terms of the Taylor series expansion of r were dropped in linearizing equation (A1) the values of c_j obtained from equations (A9) and (A10) are not the exact least-squares values. The exact values can be approached as closely as desired, however, by repeated solutions of equations (A9) and (A10) using each set of values of c_j obtained as an improved approximation for the next iteration[a].

The mathematical procedure just described is essentially that outlined in reference 20. It is the basis of the Fortran subroutine FITALL[18] which was used in this study for the solution of equations (17) and (19). FITALL requires a suitably constructed main program to supply

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[a]This statement is correct provided the solution converges properly. This will generally be the case if (1) the form of equation (A1) correctly describes the data (2) the data are not too badly scattered and (3) the first approximations of the parameters to be determined are reasonably good.

the necessary input, output, and control steps. FITALL also requires a subroutine to supply the values of r_i^0 and $\left(\frac{\partial r}{\partial c_j}\right)^0$ and the matrix inversion subroutine MATRXI.

A listing of the various programs and subprograms used in this study is given in appendix B. DRS1 is the main program for equation (17) and COSN is the corresponding subroutine. DRS2 and ELLIPSE are the main program and subroutine, respectively, for equation (19). AMAX is a function subprogram required in normalizing the raw data.

```
      PROGRAM DRS1  (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION DATA(144,3),P(20),DP(20),RES(144),CI(144),XI(144),
     2 PHI(144),I(144),RSIG(144),ARRAY(403),CNAME(12),RESPCT(144),L(4),
     3 ISTORE(144)
      REAL I,IMAX,IZERO,ISTORE
      EQUIVALENCE (XI,DATA(1,1)),(I,DATA(1,2)),(RSIG,DATA(1,3))
      EXTERNAL COSN
      LOGICAL TEST1,TEST2,TEST3
      COMMON /1/ TEST3
      COMMON COSGAM,COSPHI(144),CI
      NAMELIST/LDATA/I,XI,NDATA
      NAMELIST/PARAM/P,NP
C.....P(1)=A,P(2)=B,P(3)=M,P(4)=COS(ALPHA,S),P(5)=COS(BETA,S)
      PRINT 10
   10 FORMAT (1H1, 21HI = A*COS(PHI)**M + B)
C.....READ AND PRINT CASE IDENTIFICATION
    2 READ (5, 100) CNAME
  100 FORMAT (12A6)
      IF (EOF,5) 998,999
  999 PRINT 101, CNAME
  101 FORMAT (1H1, 12A6//)
C.....READ AND PRINT FIRST APPROXIMATION OF COEFFICIENT
      READ(5,PARAM)
      PRINT 200, (P(N), N=1,NP)
  200 FORMAT (1X, *A(0) = *, F9.6, 4X, *B(0) = *, F9.6, 4X, *M(0) = *,
     2 F9.6, 4X, *COS(ALPHA,S)(0) = *, F8.5, 4X, *COS(BETA,S)(0) = *,
     3 F8.5//)
C.....READ AND NORMALIZE DATA--SET WEIGHTING FACTOR, RSIG, TO UNITY
      READ (5,LDATA)
      IMAX=AMAX(I,NDATA)
      DO 84 K=1,NDATA
      ISTORE(K)=I(K)
      I(K)=I(K)/IMAX
   84 RSIG(K)=1.
C.....INITIALIZE PROGRAM PARAMETERS
      VAR=0
      J=1
      TEST1=.FALSE.
      TEST2=.FALSE.
      TEST3=.FALSE.
      L(1)=NDATA
      L(2)=NP
      L(3)=200
      L(4)=0
```

```
C.....SOLVE EQUATION(17) FOR LEAST-SQUARES VALUES OF COEFFICIENTS
      CALL FITALL(COSN,DATA,144,P,DP,20,Q,L,ARRAY,400)
C.....TEST SOLUTION AND PRINT APPROPRIATE ERROR MESSAGE IF NECESSARY
      IF (.NOT. TEST3) GO TO 180
      PRINT 190, L,(P(N), N=1,NP),(DP(N), N=1,NP),COSGAM,COSPHI(J)
  190 FORMAT (1X, *UNREASONABLE SOLUTION IN PROGRESS.*// 1X, *LIST = *,
     2 4I4// 1X, *P = *, 5F16.6// 1X, *DP = *, 5E16.6// 1X,
     3 *COS(GAMMA,S) = *, E16.6, 4X, *COS(PHI) = *, E16.6)
      GO TO 2
  180 IF (L(4).LE.3) GO TO 22
      PRINT 21, L
   21 FORMAT (1X, *TROUBLE IN FITALL.  LIST = *, 4I4)
      GO TO 2
   22 IF (L(4) .LE.1) GO TO 30
      PRINT 23
   23 FORMAT (1X, *CONVERGENCE CRITERION NOT SATISFIED, FOLLOWING RESULT
     2S USE BEST AVAILABLE PARAMETERS.*//)
C.....PERFORM FINAL NORMALIZATION
   30 IZERO=P(1)+P(2)
      P(1)=P(1)/IZERO
      P(2)=P(2)/IZERO
      DO 51 J=1,NDATA
      I(J)=I(J)/IZERO
      CI(J)=CI(J)/IZERO
      RES(J)=CI(J)-I(J)
      RESPCT(J)=RES(J)*100./I(J)
      VAR=VAR+RES(J)**2/(NDATA-NP)
C.....TEST COS(PHI) FOR UNREASONABLE VALUE AND PRINT VALUE AND ERROR
C.....MESSAGE IF FOUND
      IF (COSPHI(J) .LE. 1.0) GO TO 160
      PHI(J)=COSPHI(J)
      TEST1=.TRUE.
      GO TO 51
  160 PHI(J)=57.2958*ACOS(COSPHI(J))
   51 CONTINUE
      IF (TEST1) PRINT 170
  170 FORMAT (1X, *ERROR--COS(PHI) GREATER THAN ONE.*)
C.....TEST DIRECTION COSINES FOR UNREASONABLE VALUES AND PRINT
C.....APPROPRIATE ERROR MESSAGE IF NECESSARY
      SUMSQ=P(4)**2+P(5)**2
      IF (SUMSQ .LE. 1.0) GO TO 90
      PRINT 110, SUMSQ
  110 FORMAT (1X, 42HERROR--COS(ALPHA,S)**2 + COS(BETA,S)**2 = , F8.5//)
   90 IF (ABS(P(4)) .GT. 1.0) TEST2=.TRUE.
```

```
      IF (ABS(P(5)) .GT. 1.0) TEST2=.TRUE.
      IF (ABS(COSGAM) .GT. 1.0) TEST2=.TRUE.
      IF (.NOT. TEST2) GO TO 120
      PRINT 130
  130 FORMAT (1X, *ERROR--DIRECTION COSINE GREATER THAN ONE.*//)
      GO TO 140
C.....CALCULATE ALPHA(S), BETA(S), GAMMA(S), AND DELTA
  120 COSDEL=-COS(77.*1.7453E-2)*P(4)+COS(13.*1.7453E-2)*COSGAM
      DELTA=57.2958*ACOS(ABS(COSDEL))
      IF (COSDEL.LT.0) DELTA=180.-DELTA
      ALPHA=57.2958*ACOS(ABS(P(4)))
      IF (P(4).LT.0) ALPHA=180.-ALPHA
      BETA=57.2958*ACOS(ABS(P(5)))
      IF (P(5).LT.0) BETA=180.-BETA
      SGAMMA=57.2958*ACOS(COSGAM)
C.....PRINT PROGRAM TEST PARAMETER, LIST
  140 PRINT 20, L
   20 FORMAT (1X, *LIST = *, 4I4//)
C.....PRINT RESULTS
      PRINT 40, VAR
   40 FORMAT (1X, *VARIANCE = *, E14.6//)
      PRINT 50, P(1),P(2),P(3)
   50 FORMAT (1X,*A = *, F9.6, 4X, *B = *, F9.6, 4X, *M = *, F9.6//)
      PRINT 60, P(4),P(5),COSGAM
   60 FORMAT (1X, *COS(ALPHA,S) = *, F8.5, 4X, *COS(BETA,S) = *, F8.5,
     2 4X, *COS(GAMMA,S) = *, F8.5//)
      IF (TEST2) GO TO 150
      PRINT 70, ALPHA,BETA,SGAMMA,DELTA
   70 FORMAT (1X, *ALPHA(S) = *, F9.4, 4X, *BETA(S) = *, F9.4, 4X,
     2*GAMMA(S) = *, F9.4, 4X, *DELTA = *, F9.4//)
  150 PRINT 80, (PHI(J),XI(J),ISTORE(J),I(J),CI(J),RES(J),RESPCT(J),
     2 J=1,NDATA)
   80 FORMAT (37X, *NORMALIZED*/ 5X, *PHI*, 6X, *XI*, 8X, *I(EXP)*,
     2 5X, *I(EXP)*, 4X, *I(CALC)*, 4X, *RES*, 4X, *RES(PCT)*/
     3 (2F10.4, F12.6, 4F10.6))
      GO TO 2
  998 STOP
      END
```

```
      SUBROUTINE COSN(RES,DATA,NDMAX,P,DP,V,NP,J)
      REAL I
      DIMENSION DATA(NDMAX,3),P(20),DP(20)
      LOGICAL TEST3,TEST4
      COMMON /1/ TEST3
      COMMON COSGAM,COSPHI(144),CI(144)
      TEST4=.FALSE.
      XLIM=1.0E-100
C.....TEST COEFFICIENTS FOR UNREASONABLE VALUE AND SET INDICATOR IF FOUND
      IF (ABS(P(1)) .GT. 2.0) GO TO 20
      IF (ABS(P(2)) .GT. 2.0) GO TO 20
      IF (ABS(P(3)) .GT. 10.0) GO TO 20
      IF (ABS(P(4)) .GT. 1.0) GO TO 20
      IF (ABS(P(5)) .GT. 1.0) GO TO 20
C.....CONVERT XI TO RADIANS
      XI=DATA(J,1)
      RXI=XI*1.7453E-2
      I=DATA(J,2)
      V=DATA(J,3)
C.....CALCULATE COS(BETA,N)
      ARG1=SIN(76.75*1.7453E-2)**2*(1.-SIN(RXI)**2)
      IF (ARG1 .GT. XLIM) GO TO 60
      COSBETA=0.0
      GO TO 70
   60 COSBETA=SQRT(ARG1)
C.....SET SIGN OF COS(BETA,N)
      IF (XI .GT. 90. .AND. XI .LT. 270.) COSBETA=-COSBETA
C.....CALCULATE COS(GAMMA,S)
   70 ARG2=ABS(1.-P(4)**2-P(5)**2)
      IF (ARG2 .LT. XLIM) GO TO 20
      COSGAM=SQRT(ARG2)
      IF (COSGAM .GT. 1.0) GO TO 20
C.....CALCULATE COS(ALPHA,N)
      COSALPH=COS(76.75*1.7453E-2)
C.....CALCULATE COS(PHI)
      COSPHI(J)=COSALPH*P(4)+COSBETA*P(5)+COS(13.25*1.7453E-2)*COSGAM
     2 *SIN(RXI)
C.....TEST COS(PHI) FOR UNREASONABLE VALUE AND SET INDICATOR IF FOUND
      IF (ABS(COSPHI(J)) .GT. 1.0) GO TO 20
C.....TAKE ABSOLUTE VALUE OF COS(PHI) AND SET INDICATOR FOR CORRECT
C.....SIGN OF DERIVATIVES
      IF (COSPHI(J) .GE. 0) GO TO 10
      COSPHI(J)=-COSPHI(J)
      TEST4=.TRUE.
```

```
   10 CONTINUE
C.....CALCULATE PARTIAL DERIVATIVES OF I(PHI) WITH RESPECT TO COEFFICIENTS AND
C.....SET CORRECT SIGN
      DP(1)=COSPHI(J)**P(3)
      IF (ABS(DP(1)) .LT. XLIM) DP(1)=0.0
      DP(2)=1.
      IF (ABS(COSPHI(J)) .GT. XLIM)  GO TO 30
      COSPHI(J)=0.0
      DP(3)=0.0
      GO TO 40
   30 DP(3)=P(1)*COSPHI(J)**P(3)*ALOG(COSPHI(J))
   40 DP(4)=P(1)*P(3)*COSPHI(J)**(P(3)-1.)*(COSALPH-(P(4)/COSGAM)*
     2 COS(13.25*1.7453E-2)*SIN(RXI))
      IF (ABS(DP(4)) .LT. XLIM) DP(4)=0.0
      IF (TEST4) DP(4)=-DP(4)
      DP(5)=P(1)*P(3)*COSPHI(J)**(P(3)-1.)*(COSBETA-(P(5)/COSGAM)*
     2 COS(13.25*1.7453E-2)*SIN(RXI))
      IF (ABS(DP(5)) .LT. XLIM) DP(5)=0.0
      IF (TEST4) DP(5)=-DP(5)
C.....CALCULATE I(PHI)(0)
      CI(J)=P(1)*COSPHI(J)**P(3)+P(2)
C.....CALCULATE RESIDUAL OF I(PHI)
      RES=CI(J)-I
C.....TEST RESIDUAL FOR UNREASONABLE VALUE AND SET INDICATOR IF FOUND
      IF (ABS(RES) .GT. 1.0) GO TO 20
      IF (ABS(RES) .LT. XLIM) RES=0.0
      GO TO 50
   20 TEST3=.TRUE.
   50 RETURN
      END
```

```
      PROGRAM DRS2 (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION DATA(40,3),P(20),DP(20),L(4),RES(40),CI(40),XI(40),
     2 PHI(40),I(40),RSIG(40),ARRAY(403),CNAME(12),RESPCT(40),
     3 ISTORE(40)
      REAL I,IMAX,IZERO,ISTORE
      EQUIVALENCE (XI,DATA(1,1)),(I,DATA(1,2)),(RSIG,DATA(1,3))
      EXTERNAL ELLIPSE
      LOGICAL TEST1,TEST2,TEST3
      COMMON /1/ TEST3
      COMMON COSGAM,COSPHI(40),CI
      NAMELIST/LDATA/I,XI,NDATA
      NAMELIST/PARAM/P,NP
C.....P(1)=A,P(2)=B,P(3)=COS(ALPHA,S),P(4)=COS(BETA,S)
      PRINT 10
   10 FORMAT (1H1, 46HI = A*B/SQRT(A**2 + (B**2 - A**2)*COS(PHI)**2))
C.....READ AND PRINT CASE IDENTIFICATION
    2 READ (5, 100) CNAME
  100 FORMAT (12A6)
      IF (EOF,5) 998,999
  999 PRINT 101, CNAME
  101 FORMAT (1H1, 12A6//)
C.....READ AND PRINT FIRST APPROXIMATION OF COEFFICIENTS
      READ(5,PARAM)
      P(1)=1.00
      NP=4
      PRINT 200, (P(N), N=1,NP)
  200 FORMAT (1X, *A(0) = *, F9.6, 4X, *B(0) = *, F9.6, 4X,
     2 *COS(ALPHA,S)(0) = *, F8.5, 4X, *COS(BETA,S)(0) = *, F8.5//)
C.....READ AND NORMALIZE DATA--SET WEIGHTING FACTOR, RSIG, TO UNITY
      READ (5,LDATA)
      IMAX=AMAX(I,NDATA)
      DO 84 K=1,NDATA
      ISTORE(K)=I(K)
      I(K)=I(K)/IMAX
   84 RSIG(K)=1.
C.....INITIALIZE PROGRAM PARAMETERS
      VAR=0
      J=1
      TEST1=.FALSE.
      TEST2=.FALSE.
      TEST3=.FALSE.
      L(1)=NDATA
      L(2)=NP
      L(3)=200
```

```
      L(4)=0
C.....SOLVE EQUATION(19) FOR LEAST-SQUARES VALUES OF COEFFICIENTS
      CALL FITALL(ELLIPSE,DATA,40,P,DP,20,Q,L,ARRAY,400)
C.....TEST SOLUTION AND PRINT APPROPRIATE ERROR MESSAGE IF NECESSARY
      IF (.NOT. TEST3) GO TO 180
      PRINT 190, L,(P(N), N=1,NP),(DP(N), N=1,NP),COSGAM,COSPHI(J)
  190 FORMAT (1X, *UNREASONABLE SOLUTION IN PROGRESS*// 1X, *LIST = *,
     2 4I4// 1X, *P = *, 4E16.6// 1X, *DP = *, 4E16.6// 1X,
     3 *COS(GAMMA,S) = *, E16.6, 4X, *COS(PHI) = *, E16.6)
      GO TO 2
  180 IF (L(4).LE.3) GO TO 22
      PRINT 21, L
   21 FORMAT (1X, *TROUBLE IN FITALL.  LIST = *, 4I4)
      GO TO 2
   22 IF (L(4) .LE.1) GO TO 30
      PRINT 23
   23 FORMAT (1X, *CONVERGENCE CRITERION NOT SATISFIED, FOLLOWING RESULT
     2S USE BEST AVAILABLE PARAMETERS.*//)
C.....PERFORM FINAL NORMALIZATION
   30 IZERO=P(1)
      P(1)=P(1)/IZERO
      P(2)=P(2)/IZERO
      DO 51 J=1,NDATA
      I(J)=I(J)/IZERO
      CI(J)=CI(J)/IZERO
      RES(J)=CI(J)-I(J)
      RESPCT(J)=RES(J)*100./I(J)
      VAR=VAR+RES(J)**2/(NDATA-NP)
C.....TEST COS(PHI) FOR UNREASONABLE VALUE AND PRINT VALUE AND ERROR
C.....MESSAGE IF FOUND
      IF (COSPHI(J) .LE. 1.0) GO TO 160
      PHI(J)=COSPHI(J)
      TEST1=.TRUE.
      GO TO 51
  160 PHI(J)=57.2958*ACOS(COSPHI(J))
   51 CONTINUE
      IF (TEST1) PRINT 170
  170 FORMAT (1X, *ERROR--COS(PHI) GREATER THAN ONE.*)
C.....TEST DIRECTION COSINES FOR UNREASONABLE VALUES AND PRINT
C.....APPROPRIATE ERROR MESSAGE IF NECESSARY
      SUMSQ=P(3)**2+P(4)**2
      IF (SUMSQ .LE. 1.0) GO TO 90
      PRINT 110, SUMSQ
  110 FORMAT (1X, 42HERROR--COS(ALPHA,S)**2 + COS(BETA,S)**2 = , F8.5//)
```

```
   90 IF (ABS(P(3)) .GT. 1.0) TEST2=.TRUE.
      IF (ABS(P(4)) .GT. 1.0) TEST2=.TRUE.
      IF (ABS(COSGAM) .GT. 1.0) TEST2=.TRUE.
      IF (.NOT. TEST2) GO TO 120
      PRINT 130
  130 FORMAT (1X, *ERROR--DIRECTION COSINE GREATER THAN ONE.*//)
      GO TO 140
C.....CALCULATE ALPHA(S), BETA(S), GAMMA(S), AND DELTA
  120 COSDEL=-COS(77.*1.7453E-2)*P(3)+COS(13.*1.7453E-2)*COSGAM
      DELTA=57.2958*ACOS(ABS(COSDEL))
      IF (COSDEL.LT.0) DELTA=180.-DELTA
      ALPHA=57.2958*ACOS(ABS(P(3)))
      IF (P(3) .LT. 0) ALPHA=180.-ALPHA
      BETA=57.2958*ACOS(ABS(P(4)))
      IF (P(4) .LT. 0) BETA=180.-BETA
      SGAMMA=57.2958*ACOS(COSGAM)
C.....PRINT PROGRAM TEST PARAMETER, LIST
  140 PRINT 20, L
   20 FORMAT (1X, *LIST = *, 4I4//)
C.....PRINT RESULTS
      PRINT 40, VAR
   40 FORMAT (1X, *VARIANCE = *, E14.6//)
      PRINT 50, P(1),P(2)
   50 FORMAT (1X, *A = *, F9.6, 4X, *B = *, F9.6//)
      PRINT 60, P(3),P(4),COSGAM
   60 FORMAT (1X, *COS(ALPHA,S) = *, F8.5, 4X, *COS(BETA,S) = *, F8.5,
     2 4X, *COS(GAMMA,S) = *, F8.5//)
      IF (TEST2) GO TO 150
      PRINT 70, ALPHA,BETA,SGAMMA,DELTA
   70 FORMAT (1X, *ALPHA(S) = *, F9.4, 4X, *BETA(S) = *, F9.4, 4X,
     2*GAMMA(S) = *, F9.4, 4X, *DELTA = *, F9.4//)
  150 PRINT 80, (PHI(J),XI(J),ISTORE(J),I(J),CI(J),RES(J),RESPCT(J),
     2 J=1,NDATA)
   80 FORMAT (37X, *NORMALIZED*/ 5X, *PHI*, 6X, *XI*, 8X, *I(EXP)*,
     2 5X, *I(EXP)*, 4X, *I(CALC)*, 4X, *RES*, 4X, *RES(PCT)*/
     3 (2F10.4, F12.6, 4F10.6))
      GO TO 2
  998 STOP
      END
```

```
      SUBROUTINE ELLIPSE(RES,DATA,NDMAX,P,DP,V,NP,J)
      REAL I
      DIMENSION DATA(NDMAX,3),P(20),DP(20)
      LOGICAL TEST3
      COMMON /1/ TEST3
      COMMON COSGAM,COSPHI(40),CI(40)
      XLIM=1.0E-100
C.....TEST COEFFICIENTS FOR UNREASONABLE VALUE AND SET INDICATOR IF FOUND
      IF (ABS(P(1)) .GT. 2.0) GO TO 20
      IF (ABS(P(2)) .GT. 2.0) GO TO 20
      IF (ABS(P(3)) .GT. 1.0) GO TO 20
      IF (ABS(P(4)) .GT. 1.0) GO TO 20
C.....CONVERT XI TO RADIANS
      XI=DATA(J,1)
      RXI=XI*1.7453E-2
      I=DATA(J,2)
      V=DATA(J,3)
C.....CALCULATE COS(BETA,N)
      ARG1=SIN(76.75*1.7453E-2)**2*(1.-SIN(RXI)**2)
      IF (ARG1 .LT. XLIM) GO TO 20
      COSBETA=SQRT(ARG1)
C.....SET SIGN OF COS(BETA,N)
      IF (XI .GT. 90. .AND. XI .LT. 270.) COSBETA=-COSBETA
C.....CALCULATE COS(GAMMA,S)
      ARG2=ABS(1.-P(3)**2-P(4)**2)
      IF (ARG2 .LT. XLIM) GO TO 20
      COSGAM=SQRT(ARG2)
      IF (COSGAM .GT. 1.0) GO TO 20
C.....CALCULATE COS(ALPHA,N)
      COSALPH=COS(76.75*1.7453E-2)
C.....CALCULATE COS(PHI)
      COSPHI(J)=COSALPH*P(3)+COSBETA*P(4)+COS(13.25*1.7453E-2)*COSGAM
     2 *SIN(RXI)
C.....TEST COS(PHI) FOR UNREASONABLE VALUE AND SET INDICATOR IF FOUND
      IF (ABS(COSPHI(J)) .GT. 1.0) GO TO 20
C.....CALCULATE INTERMEDIATE FUNCTIONS TO BE USED BELOW
      SINSQ=(1.-COSPHI(J)**2)
      ARG3=P(1)**2+(P(2)**2-P(1)**2)*COSPHI(J)**2
      IF (ARG3 .LT. 0.) GO TO 20
      VAL1=SQRT(ARG3)
      IF (VAL1 .LT. XLIM) GO TO 20
      VAL2=-P(1)*P(2)*(P(2)**2-P(1)**2)*COSPHI(J)
      VAL3=COS(13.25*1.7453E-2)*SIN(RXI)/COSGAM
C.....CALCULATE PARTIAL DERIVATIVES OF I(PHI) WITH RESPECT TO COEFFICIENTS
```

```
      DP(1)=P(2)/VAL1-P(1)**2*P(2)*SINSQ/VAL1**3
      IF (ABS(DP(1)) .LT. XLIM) DP(1)=0.0
      DP(2)=P(1)/VAL1-P(1)*P(2)**2*COSPHI(J)**2/VAL1**3
      IF (ABS(DP(2)) .LT. XLIM) DP(2)=0.0
      DP(3)=VAL2/VAL1**3*(COSALPH-VAL3*P(1))
      IF (ABS(DP(3)) .LT. XLIM) DP(3)=0.0
      DP(4)=VAL2/VAL1**3*(COSBETA-VAL3*P(2))
      IF (ABS(DP(4)) .LT. XLIM) DP(4)=0.0
C.....CALCULATE I(PHI)(0)
      CI(J)=P(1)*P(2)/VAL1
C.....CALCULATE RESIDUAL OF I(PHI)
      RES=CI(J)-I
C.....TEST RESIDUAL FOR UNREASONABLE VALUE AND SET INDICATOR IF FOUND
      IF (ABS(RES) .GT. 1.0) GO TO 20
      IF (ABS(RES) .LT. XLIM) RES=0.0
      GO TO 50
   20 TEST3=.TRUE.
   50 RETURN
      END
```

```
      SUBROUTINE FITALL(RESID,X,NDMAX,P,DP,MAX,Q,LIST,HOLD,MMAX)
      DIMENSION P(20),DP(20),LIST(4),A(20,20),S(400),HOLD(403),B(20),
     2 IS(3)
      EQUIVALENCE (IS(1),KK),(IS(2),NFIX),(IS(3),KSIG),(S(1),A(1,1))
      DATA CONV/0.001/
      LOGICAL TEST3
      COMMON /1/ TEST3
C.....INITIALIZE
      JJ=LIST(1),
      KK=LIST(2),
      LOOPS=LIST(3),
      LIST(3)=0
      NFREE=JJ-KK,
      IF(LOOPS.EQ.0)GO TO 10,
      MOST=2*KK,
      IF(KK.LT.1.OR.NFREE.LT.0)GO TO 14
      IF(KK.GT.MAX)GO TO 15,
C.....BEGIN ITERATION LOOP
    1 NFIX=KK,
      DO 2 N=1,MAX,
      B(N)=0.,
      DO 2 M=1,MAX,
    2 A(M,N)=0.,
      DO 6 J=1,JJ,
      CALL RESID(R,X,NDMAX,P,DP,VAR,KK,
      IF (TEST3) GO TO 29
      IF(VAR.NE.0.)GO TO 4,
      NFIX=NFIX+1,
      IF(NFIX.GT.MAX)GO TO 15,
      IF(NFIX.GT.MOST)GO TO 14,
C.....CALCULATE FIX POINT ELEMENTS
      B(NFIX)=R
      DO 3 M=1,KK
      A(M,NFIX)=DP(M)
    3 A(NFIX,M)=DP(M)
      GO TO 6
C.....CALCULATE REGULAR POINT
    4 DO 5 N=1,KK
      B(N)=B(N)+R*DP(N)/VAR,
      DO 5 M=N,KK
    5 A(M,N)=A(M,N)+DP(M)*DP(N)/VAR,
    6 CONTINUE
C.....FINISH OFF MATRIX
      DO 7 N=1,KK
```

```
      DO 7 M=N,KK
    7 A(N,M)=A(M,N)
C.....INVERT MATRIX
      KSIG=0
      CALL IMATINV(A,MAX,NFIX,DET,KSIG)
      IF(KSIG.EQ.1.OR.KSIG.EQ.2)GO TO 16
      IF(LOOPS.EQ.-1)GO TO 10
C.....CALCULATE NEW VALUES OF PARAMETERS
      BIG=0.
      DO 9 M=1,KK
      SUM=0.
      DO 8 N=1,NFIX
    8 SUM=SUM-A(M,N)*B(N)
      P(M)=P(M)+SUM
    9 BIG=BIG+AMAX1(ABS(SUM)-CONV*ABS(P(M)),0.)
      LIST(3)=LIST(3)+1
      IF(BIG.EQ.0.)GO TO 10
      IF(LIST(3).GE.LOOPS)GO TO 17
      GO TO 1
C.....CONVERGENCE ACHIEVED -- COMPUTE VARI
   10 IF(LOOPS.EQ.1)GO TO 18
      Q=0.
      SUM=0.
      DO 11 J=1,JJ
      CALL RESID(R,X,NDMAX,P,DP,VAR,KK,J)
      IF(VAR.EQ.0.)GO TO 11
      SUM=SUM+R*R/VAR
   11 CONTINUE
      Q=SQRT(SUM/FLOAT(NFREE))
      IF(KSIG.NE.0)GO TO 19
      GO TO 50
   14 LIST(4)=LIST(4)+1
   15 LIST(4)=LIST(4)+1
   16 LIST(4)=LIST(4)+1
   17 LIST(4)=LIST(4)+1
   18 LIST(4)=LIST(4)+1
   19 LIST(4)=LIST(4)+1
C.....ENTRY FOR SAVING MATRIX
      ENTRY FITSAV
   50 DO 20 N=1,MMAX
   20 HOLD(N+3)=S(N)
      DO 27 N=1,3
   27 HOLD(N)=IS(N)
      RETURN
```

```
C.....ENTRY FOR RESTORING SAVED MATRIX
      ENTRY FITBAK
      DO 21 N=1,MMAX
   21 S(N)=HOLD(N+3)
      DO 28 N=1,3
   28 IS(N)=HOLD(N)
   29 RETURN
```

```
      SUBROUTINE  MATRXI(X,MMAX,MX,DET,KSIG)
C.....SUBROUTINE FOR OBTAINING DETERMINANT OF INPUT MATRIX
      DIMENSION X(20,20),Y(20,20),Z(2,20,20),K(20)
      LOGICAL MATIN
      EQUIVALENCE (Y,Z)
      DOUBLE PRECISION A,R,PROD,Y,
      DATA DELT,EPS,LOOPS/0.0001,1.E-0.,
      GO TO 711
C.....MATRIX INVERSION BY GAUSS-JORDAN ELIMINATION
      ENTRY IMATINV
      MATIN=.TRUE.
      GO TO 1
  711 MATIN=.FALSE.
    1 DO 405 I=1,2
      DO 405 J=1,20
      DO 405 ICNT=1,20
      Z(I,J,ICNT)=0.
  405 CONTINUE
C.....INITIALIZE ROUTINE AND TEST MX (=ORDER OF MATRIX)
      M=MX,
      IF(M.GT.1.AND.M.LE.MMAX)GO TO 5,
      IF(M.EQ.1)GO TO 2,
      KSIG=KSIG+1,
      RETURN
    2 PROD=X(1,1),
      IF(PROD.NE.0.)GO TO 4,
    3 KSIG=KSIG+2,
      RETURN
    4 X(1,1)=1./PROD,
      GO TO 23
    5 PROD=1.,
      MM=M-1,
      DO 6 I=1,M,
      K(I)=I,
      DO 6 J=1,M,
    6 Y(I,J)=X(I,J),
C.....BEGIN BY FINDING LARGEST PIVOTAL ELEMENT
      DO 11 I=1,M,
      A=0.,
      DO 7 J=I,M,
      IF(DABS(Y(J,1)).LE.A)GO TO 7
      A=DABS(Y(J,1))
      L=J,
    7 CONTINUE
```

```
      IF(A.EQ.0.)GO TO 3.
C.....REARRANGE ROWS AND ORDER ARRAY
      N=K(L).
      K(L)=K(I).
      K(I)=N.
      DO 8 J=1.M.
      A=Y(I.J).
      Y(I.J)=Y(L.J).
    8 Y(L.J)=A.
C.....REDUCE PIVOTAL ROW
      A=Y(I.1).
      IF(.NOT.MATIN)PROD=PROD*A
      DO 9 J=1.MM.
    9 Y(I.J)=Y(I.J+1)/A.
      Y(I.M)=1./A.
C.....REDUCE REMAINING ROWS
      DO 11 L=1.M.
      IF(L.EQ.I)GO TO 11.
      A=Y(L.I).
      DO 10 N=1.MM.
      Y(L.N)=Y(L.N+1)-A*Y(I.N).
      IF(DABS(Y(L.N)).LT.(DABS(Y(L.N+1))*EPS))Y(L.N)=0.
   10 CONTINUE.
      Y(L.M)=-A*Y(I.M).
   11 CONTINUE
C.....UNSCRAMBLE INVERTED MATRIX
      DO 15 I=1.M.
      IF(K(I).EQ.I)GO TO 15.
      PROD=-PROD.
      DO 12 J=I.M.
      IF(K(J).EQ.I)GO TO 13.
   12 CONTINUE.
      GO TO 3
   13 DO 14 L=1.M.
      A=Y(L.I).
      Y(L.I)=Y(L.J).
   14 Y(L.J)=A.
      K(J)=K(I).
   15 CONTINUE
C.....OBTAIN ERROR MATRIX
      DO 20 N=1.LOOPS.
      TEST=0..
      DO 17 I=1.M.
      DO 17 J=1.M.
```

```
      R=0.,
      DO 16 L=1,M,
   16 R=R-Z(1,L,J)*X(I,L),
      IF(I.EQ.J)R=R+1.,
      ABSR=SNGL(DABS(R))
      TEST=AMAX1(TEST,ABSR)
   17 Z(2,I,J)=R,
      DO 19 I=1,M,
      DO 19 J=1,M,
      A=0.,
      DO 18 L=1,M,
   18 A=A+Z(1,I,L)*Z(2,L,J),
      Z(1,I,J)=Z(1,I,J)+A,
   19 CONTINUE,
      IF(TEST.LE.DELT)GO TO 21,
   20 CONTINUE
      KSIG=KSIG+3,
C.....TRANSFER FINAL INVERSE
   21 DO 22 I=1,M,
      DO 22 J=1,M,
   22 X(I,J)=Z(1,I,J),
   23 DET=PROD,
      RETURN
      END
```

```
      FUNCTION AMAX(A,N)
      DIMENSION A(144)
      AMAX=A(1)
      DO 70 M=2,N
      IF(A(M)-AMAX)70,70,60
   60 AMAX=A(M)
   70 CONTINUE
      RETURN
      END
```

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